

On the Solution of the Self-Interaction Problem in Kohn-Sham Density Functional Theory

M. Däne,^{1,2} A. Gonis,¹ D. M. Nicholson,³ and G. M. Stocks²

¹*Physical and Life Sciences, Lawrence Livermore National Laboratory, PO Box 808, L-372, Livermore, CA 94551*

²*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831*

³*Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831*

We report on a methodology for the treatment of the Coulomb energy and potential in Kohn-Sham density functional theory that is free from self-interaction effects. Specifically, we determine the Coulomb potential given as the functional derivative of the Coulomb energy with respect to the density, where the Coulomb energy is calculated explicitly in terms of the pair density of the Kohn-Sham orbitals. An orthonormal and complete basis that is an explicit functional of the density is used to perform the functional differentiation. This leads to a new formalism that provides an analytic, closed-form determination of the exchange potential. This method is applied to one-dimensional model systems and to the atoms Helium through Krypton based on an exchange only implementation. We compare and contrast the results of the present method with those obtained in the Hartree-Fock formalism and within the optimized effective potential method.

PACS numbers: 31.10.+z, 31.15.eg, 31.15.vj, 31.50.Df

Keywords: electronic structure theory, exchange energy, exchange potential, density functional theory, local density approximation, electron correlation, self-interaction free, exact exchange

I. INTRODUCTION

Modern calculations of the electronic structure of condensed matter rest on density functional theory¹⁻⁴ (DFT), whose implementation is carried out within various forms based on the Kohn-Sham (KS) formulation of the theory⁵. While there is a vast body of work that attests to the utility of this approach, it has well documented failures in predicting electronic structure and related properties of materials where the effects of the Coulomb interaction are judged to be particularly strong. Such materials include, but are not limited to, 3d-transition metal oxides, 4f-electron rare earths and 5f-electron actinide systems. An important factor in this failure is the presence of the well-known unphysical self-interaction terms in the Hartree (classical) expression for the Coulomb energy as well as in the exchange and correlation energy functional. While there have been numerous attempts⁶⁻¹⁷ to correct for the presence of self-interaction, no fully satisfactory coherent scheme has yet emerged (for a at least a partial compendium of methods, see¹⁸).

Self-interaction was introduced into the theory through the original formulation of the so-called local density approximation (LDA) or local spin-density approximation (LSDA)³⁻⁵, including their gradient corrected versions (GGAs), in which the Coulomb energy of the interacting particles is expressed as that of a classical charge distribution, $n(\mathbf{r})$, with itself,

$$U_{\text{cl}} = \frac{1}{2} \int \int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (1)$$

An advantage of the classical form (Hartree term) is its explicit dependence on the density that allows the functional differentiation with respect to the density and the determination of its contribution to the potential. Even though the problematic nature of the Hartree term was realized from the beginning, most of the currently used energy functionals¹⁸ are still based on it. The presence of self-interaction reduces not only the reliability and convincing power of results obtained in the

LDA, but also affects the formal standing of the theory as a whole.

Among the functional forms cited in¹⁸, some⁶⁻¹⁷ stand out as strong candidates for the development of a general theory for a self-interaction free formulation of KS-DFT. Prominent among these are the self-interaction correction (SIC) method⁸, and the optimized effective potential (OEP) method^{6,7,15}. The former corrects for self-interaction on an orbital by orbital basis, but cannot be shown to remove the SI error completely⁸. The latter relies on the treatment of so-called orbital dependent functionals and attempts a functional differentiation of the Coulomb energy by means of a chain rule based on the v -representability of the density.

It is well known that self-interaction does not arise when the Coulomb energy is calculated in terms of the pair density, a quantity that in the KS formulation of DFT is determined through the Slater determinant of the KS orbitals. However, the dependence of the pair density on the density is only implicit. In one implementation of the OEP method, this implicit behavior is attacked through the chain rule of functional derivatives which, in turn, involves the calculation of the (inverse) susceptibility of the KS system⁷. Alternative procedures, such as the parametrization of the potential^{12,19} have been formulated, where the coefficients are determined to minimize the energy. Results obtained in the two methods are compared with those of the present procedure in a latter section.

In this paper, we provide a new and alternative formulation that eliminates self-interaction effects by construction, preventing their appearance through the treatment of the exchange term that is functionally differentiated with respect to the density to produce the exchange potential. Combined with the so-called Hartree term, this leads to a Coulomb potential that is determined as the functional derivative of the Coulomb energy, properly expressed in terms of the pair density, with respect to the density. We refer to the new method throughout the paper as self-interaction free (SIF). The formalism relies on a novel mathematical procedure in which a function, e.g.,

the KS orbitals, that depends implicitly on the density, can be expanded in an orthonormal and complete basis of functions whose elements are expressed explicitly in terms of the density. As demonstrated in the paper, functional derivatives of the occupied KS orbitals can be obtained through term by term differentiation of the expanded forms, not requiring the calculation of the susceptibility or its inverse. The final forms of the functional derivatives are expressed analytically in terms of the gradients of the occupied orbitals, whose numerical evaluation is straightforward.

A short introduction of the method has been presented in previous work²⁰. In the following pages, we provide complete details of the technical, that is algebraic, and computational components of this method that show both the simplicity of the formalism as well as the power that derives from it. We demonstrate the characteristic features and efficacy of the new method by means of model one-dimensional calculations as well as calculations of the exchange potential and energies of the ground states of atomic systems from Helium to Krypton. We compare some of our results with the corresponding ones obtained in the OEP and Hartree-Fock (HF) methodologies, and comment on the differences between the results of the calculations.

This is a rather long paper because of our intention of providing as complete and detailed an exposition of the method as possible. The paper takes the following form.

In Section II, we provide a derivation of the KS equations identifying explicitly the terms corresponding to the correlation energy and potential, the exchange potential determined in a local approximation to the KS equations, and point out the difficulties associated with self-interaction. Subsection II C states the quantum mechanically correct form of the Coulomb energy to be used in the KS formalism. The equidensity basis, the formal and computational foundation of the methodology introduced here is set forth in Section III. The application of the formalism to model and realistic atomic system is presented in Section IV. Differences between the method provided in this paper and others are discussed in Section V. Section VI contains our conclusions.

In the interests of completeness, we also provide in the form of a set of extended appendices detailed derivations of key expressions resulting from our formulation that we used in calculating the results presented in the main part of the paper.

II. KOHN-SHAM EQUATIONS

In order to clarify the SIF methodology and its effectiveness in treating a self-interaction free Coulomb energy, we briefly review the basics of KS density functional theory^{1,5}. We consider a finite number, N , of electrons interacting via a Coulomb repulsion confined in a volume, Ω , and moving under the action of an external potential, $v(\mathbf{r})$. For simplicity, in the following we consider only non-degenerate states and in much of the development we suppress the presence of spin. Final expressions, however, are given in full spin-resolved form (see appendices).

A. Kohn-Sham Equations for Ground States

The Hamiltonian describing an interacting system of N electrons in an external potential takes the usual form,

$$\hat{H}^N = \hat{v} + \hat{T}^N + \hat{U}^N, \quad (2)$$

with the operators \hat{v} , \hat{T}^N and \hat{U}^N corresponding, respectively, to the external field, the kinetic energy and the inter-particle interaction (Coulomb repulsion). The ground-state energy of the system is given by the expectation value,

$$E_g = \langle \Psi_g^N | \hat{H}^N | \Psi_g^N \rangle, \quad \langle \Psi_g^N | \Psi_g^N \rangle = 1, \quad (3)$$

where $|\Psi_g^N\rangle$ denotes the many-particle ground state of \hat{H}^N . For electrons, $|\Psi_g^N\rangle$ leads to a wave function, $\Psi_g^N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, that is antisymmetric with respect to interchange of the coordinates (and spins) of individual particles, according to the requirements of Fermi statistics. We use the notation, $|\Psi^N\rangle \rightarrow n(\mathbf{r})$, and say $|\Psi^N\rangle$ leads to $n(\mathbf{r})$, to denote the property,

$$n(\mathbf{r}) = N \int |\Psi^N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N, \quad (4)$$

where $n(\mathbf{r})$ denotes the single-particle density function normalized to the total number of particles, N . This property is formally equivalent to taking the expectation value with respect to $\Psi_g^N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ of the single-particle number operator, $\hat{n}(\mathbf{r}) = \psi^\dagger(\mathbf{r})\psi(\mathbf{r})$, where ψ^\dagger and ψ are field creation and destruction operators for an electron at \mathbf{r} . We now write (3) in the form,

$$E_g = \int v(\mathbf{r})n_g(\mathbf{r})d\mathbf{r} + \langle \Psi_g^N | \hat{T} + \hat{U} | \Psi_g^N \rangle = \underbrace{\text{Min}}_{n(\mathbf{r})} \left[\int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n] \right] = \underbrace{\text{Min}}_{n(\mathbf{r})} E[n], \quad (5)$$

in terms of the constrained search functional^{21,22},

$$F[n] = \underbrace{\text{Min}}_{|\Psi\rangle \rightarrow n(\mathbf{r})} \langle \Psi | \hat{T}^N + \hat{U}^N | \Psi \rangle. \quad (6)$$

Given a density, $n(\mathbf{r})$, the constrained search examines all antisymmetric N -particle wave functions that lead to the density and delivers the state (in the absence of degeneracy) that produces the minimum value of $\langle \Psi^N | \hat{T}^N + \hat{U}^N | \Psi^N \rangle$. Cioslowski²³ has provided a formal procedure for generating all antisymmetric wave functions leading to $n(\mathbf{r})$ and identifying that $\Psi_0^N(\mathbf{r}_1, \dots, \mathbf{r}_N)$ (in the absence of degeneracy) that determines $F[n]$. For v -representable densities, $F[n]$ gives the Hohenberg and Kohn functional¹, $F_{\text{HK}}[n]$, and the minimizing state $|\Psi_0^N\rangle$ coincides with $|\Psi_g^N\rangle$.

For any other anti-symmetric state (wave function) $|\Phi^N\rangle \neq |\Psi_g^N\rangle$ such that $|\Phi^N\rangle \rightarrow n(\mathbf{r})$, we have,

$$F[n] \leq \langle \Phi^N | \hat{T} + \hat{U} | \Phi^N \rangle, \quad (7)$$

so that the exact ground-state energy, E_g , forms a lower bound of the expectation values of the Hamiltonian with respect to antisymmetric N -particle states, $|\Phi^N\rangle \rightarrow n(\mathbf{r})$.

As in the initial formulation of DFT by Kohn and Sham⁵, we postulate the existence of a *fictitious* non-interacting N -particle system described by the Hamiltonian,

$$\hat{H}_s^N = \hat{v}_s + \hat{T}^N, \quad (8)$$

under the action of an external potential, \hat{v}_s , whose ground-state density is identical to the density of the interacting system described by \hat{H}^N . In analogy with (6), we define the constrained search functional,

$$T_s[n] = \underset{|\Phi^N\rangle \rightarrow n(\mathbf{r})}{\text{Min}} \langle \Phi^N | \hat{T}^N | \Phi^N \rangle. \quad (9)$$

In the absence of degeneracy, the minimizing $|\Phi_s^N\rangle$ is a single Slater determinant²² (denoted by the subscript s) of order N .

Because generally, $|\Phi_s^N\rangle \neq |\Psi_g^N\rangle$, we have,

$$E_s = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F_s[n] \geq E_g, \quad (10)$$

where

$$F_s[n] = \langle \Phi_s^N | \hat{T}^N + \hat{U}^N | \Phi_s^N \rangle \geq F[n]. \quad (11)$$

Defining the quantity, $E_c[n] = F[n] - F_s[n]$, and adding and subtracting $F_s[n]$ to $E[n]$ in Eq. (5), we obtain,

$$E[n] = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F_s[n] + E_c[n]. \quad (12)$$

The quantity $E_c[n]$ is referred to as the *correlation energy*. We can view the last expression as a means of determining E_g through the states of the non-interacting system, $|\Phi_s^N\rangle$, given the functional difference, $E_c[n]$.

The Slater determinant, $|\Phi_s^N\rangle$, is obtained from the solutions of a single-particle Schrödinger equation, which then also defines the potential, $v_s(\mathbf{r})$,

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) \right] f_i(\mathbf{r}) = \epsilon_i f_i(\mathbf{r}). \quad (13)$$

From (4) it follows that,

$$n(\mathbf{r}) = \sum_{j=1}^N |f_j(\mathbf{r})|^2, \quad (14)$$

where the orbitals, $f_j(\mathbf{r})$, correspond to the N eigenvalues of (13) that lie the lowest in energy. With respect to the same states, we also define the pair density for the non-interacting system,

$$n_s(\mathbf{r}_1, \mathbf{r}_2) = \binom{N}{2} \int |\Phi^N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_3 \dots d\mathbf{r}_N \quad (15)$$

$$= \frac{1}{2} \sum_{i,j}^N |f_i(\mathbf{r}_1)f_j(\mathbf{r}_2) - f_j(\mathbf{r}_1)f_i(\mathbf{r}_2)|^2. \quad (16)$$

Now, the functional $F_s[n]$ takes the form,

$$F_s[n] = \sum_i \int d\mathbf{r} f_i^*(\mathbf{r}) \left[-\frac{1}{2}\nabla_{\mathbf{r}}^2 \right] f_i(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{n_s(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (17)$$

The form of $F_s[n]$ is expressed in terms of the fully exchanged two-particle density and is by construction free of self-interaction effects. From Eq. (13) we obtain the expectation value of the kinetic energy operator,

$$\begin{aligned} T_s[n] &= \sum_i \int d\mathbf{r} f_i^*(\mathbf{r}) \left[-\frac{1}{2}\nabla_{\mathbf{r}}^2 \right] f_i(\mathbf{r}) \\ &= \sum_i \epsilon_i \int d\mathbf{r} f_i^*(\mathbf{r})f_i(\mathbf{r}) - \int d\mathbf{r} v_s(\mathbf{r})n(\mathbf{r}) \\ &= \sum_i \epsilon_i - \int d\mathbf{r} v_s(\mathbf{r})n(\mathbf{r}), \end{aligned} \quad (18)$$

where a star denotes the complex conjugate of a quantity.

Using these expressions, we can write

$$\begin{aligned} E_c[n] &= F[n] - F_s[n] \\ &= (T[n] - T_s[n]) \\ &\quad + \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{n(\mathbf{r}_1, \mathbf{r}_2; [n]) - n_s(\mathbf{r}_1, \mathbf{r}_2; [n])}{|\mathbf{r}_1 - \mathbf{r}_2|}, \end{aligned} \quad (19)$$

where T denotes the exact expectation value of the kinetic energy of the interacting system and $n(\mathbf{r}_1, \mathbf{r}_2)$ is the corresponding exact two-particle density.

Using the stationarity property of the KS energy for the ground state with respect to the density¹⁻⁴, $\frac{\delta E_g[n]}{\delta n(\mathbf{r})} \Big|_{n=n_g} = 0$ and $\frac{\delta T_s[n]}{\delta n(\mathbf{r})} = -v_s(\mathbf{r}) + c$ ^{3,4} (where in the following the constant c is suppressed), we obtain the requirement at the ground state,

$$v_s(\mathbf{r}) = v(\mathbf{r}) + \left[\frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\frac{\delta n_s(\mathbf{r}_1, \mathbf{r}_2)}{\delta n(\mathbf{r})}}{|\mathbf{r}_1 - \mathbf{r}_2|} + \mu_c(\mathbf{r}) \right]_{n=n_g}, \quad (20)$$

where the terms in the square brackets are the sum of the Coulomb potential and the correlation potential,

$$\mu_c(\mathbf{r}) = \frac{\delta E_c[n]}{\delta n(\mathbf{r})}, \quad (21)$$

completing the expression for v_s to be used in Eq. (13). Equation (20) gives a unique KS potential, leaving no freedom in its determination: It is the unique (generally within a constant) potential that leads to the density.

The quantity $E_c[n]$ appearing in the previous discussion is exact, but generally unknown. For the case of systems with infinite numbers of electrons, a correlation energy functional that is consistent with the second Hohenberg-Kohn theorem

in yielding energies that are no lower than their experimental counterparts can be constructed based on the properties of the homogeneous electron gas (jellium), as developed in the work of Ceperley and Alder²⁴. For finite systems, such a consistent construction of the correlation energy is still lacking. In the following, we set this term equal to zero and concentrate on what is known as the *exchange only* form of the KS functional (the nomenclature to become clear below), that takes the form,

$$\tilde{E}[n] = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F_s[n] \geq E_g. \quad (22)$$

Our aim is to develop a methodology that, with $\mu_c(\mathbf{r})$ set equal to zero, determines the potential (KS potential), $v_s(\mathbf{r})$, within the exchange-only mode of implementation of the theory, through the derivative of the Coulomb energy with respect to the density including the exchange term.

B. Hartree Approximation of the Coulomb Energy

In the local-density approximation (LDA)⁵, the Coulomb energy of an interacting N -particle system, e.g., an atom, is approximated by the classical expression,

$$U_{cl} = \frac{1}{2} \int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \quad (23)$$

where $n(\mathbf{r})$ denotes the ground-state density of the interacting system, a form that lends itself immediately to functional differentiation with respect to $n(\mathbf{r})$, (the density appears explicitly inside the integral).

Computational ease, however, comes at a high price: the product of densities allows the simultaneous occupation of the same orbital by a single electron, in violation of the Pauli exclusion principle. Alternatively, an electron at position \mathbf{r}_1 is allowed to interact with itself at \mathbf{r}_2 , leading to a clearly unphysical *self-interaction effect*.

C. Coulomb Exact-Exchange Kohn-Sham Functional

Within the KS formulation, the quantum-mechanically correct expression of the Coulomb repulsion energy of an non-interacting N -particle system takes the form,

$$U_{QM} = \frac{1}{2} \int \frac{n_s(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \quad (24)$$

where $n_s(\mathbf{r}_1, \mathbf{r}_2)$ is the pair density obtained from the KS orbitals. In general, it is convenient to define the exchange term,

$$J_s(\mathbf{r}_1, \mathbf{r}_2) = n_s(\mathbf{r}_1, \mathbf{r}_2) - n(\mathbf{r}_1)n(\mathbf{r}_2), \quad (25)$$

and a corresponding *exchange energy*,

$$J_s = \frac{1}{2} \int \frac{J_s(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (26)$$

In this case, with $f_j(\mathbf{r})$ denoting an orbital in the KS determinant, the pair density takes the form (σ denotes spin),

$$n_s(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \sum_{i,j} |f_i(\mathbf{r}_1) f_j(\mathbf{r}_2) - f_j(\mathbf{r}_1) f_i(\mathbf{r}_2)|^2 \quad (27)$$

$$= \frac{1}{2} \sum_{i,j} \left[f_{i,\sigma_i}^*(\mathbf{r}_1) f_{j,\sigma_j}^*(\mathbf{r}_2) f_{i,\sigma_i}(\mathbf{r}_1) f_{j,\sigma_j}(\mathbf{r}_2) - f_{i,\sigma_i}^*(\mathbf{r}_1) f_{j,\sigma_j}^*(\mathbf{r}_2) f_{j,\sigma_j}(\mathbf{r}_1) f_{i,\sigma_i}(\mathbf{r}_2) \delta_{\sigma_i, \sigma_j} \right], \quad (28)$$

and the exchange term has the form,

$$J_s(\mathbf{r}_1, \mathbf{r}_2) = - \sum_{i,j} \left[f_{i,\sigma_i}^*(\mathbf{r}_1) f_{j,\sigma_j}^*(\mathbf{r}_2) f_{j,\sigma_j}(\mathbf{r}_1) f_{i,\sigma_i}(\mathbf{r}_2) \delta_{\sigma_i, \sigma_j} \right]. \quad (29)$$

Finally, the exchange contribution to the single-particle potential arising from the Coulomb energy, called the exchange potential v_x , can be written as,

$$v_x(\mathbf{r}) = \frac{\delta J_s[n]}{\delta n(\mathbf{r})}, \quad (30)$$

in which the functional dependence on the density is explicitly indicated.

Written in terms of the expression in (27), the energy functional to be minimized in the exchange-only form of the KS formulation of ground-state DFT takes the form,

$$E[n] = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + T_s[n] + U_{cl}[n] + J_s[n]. \quad (31)$$

This form exhibits clearly the difficulty that has been encountered in attempts to implement the KS formulation of DFT. While the functional differentiation of the Hartree term with respect to the density is straightforward (explicit dependence on density under the integral), the orbitals that enter the definition of the exchange term are only implicitly dependent on the density defying immediate differentiation with respect to $n(\mathbf{r})$ by analytic means. Even a brief survey of the many forms proposed for bypassing this seemingly impossible task would be exceedingly lengthy and take us too far afield of our intended purpose. At the same time, a few comments are in order.

The OEP method^{6,7} is the best known and most widely used procedure for the solution of the KS equations in the presence of exact exchange. The functional differentiation of the Coulomb energy in reconstructing the potential within the OEP method is computationally intensive, usually involving the calculation of the inverse susceptibility and ultimately requiring the solution of an integral equation. Alternatively, the potential can be parametrized^{12,19} where parameters are determined in order to minimize the energy. The present SIF method avoids the need to solve the OEP equations, by using a strictly analytic treatment in obtaining the functional derivative of the Coulomb energy with respect to the density. This is accomplished through the use of the equidensity basis formalism, introduced by Macke²⁵ and Harriman²⁶. In addition

to orthonormality, Zumbach and Maschke²⁷ proved that the basis is complete. The expansion of the orbitals in this basis brings out the explicit dependence on the density allowing the straightforward differentiation using the product rule. The existence of the basis has been known for some time, but as far as we are aware the use proposed here has not been attempted.

III. EQUIDENSITY BASIS

The calculation of the Coulomb potential in Eq. (20) requires the functional derivative of the non-interacting pair density $n_s(\mathbf{r}_1, \mathbf{r}_2)$ with respect to the (spin) density $n^\sigma(\mathbf{r})$. This can be performed analytically by expressing the former in terms of an expansion that exhibits explicitly the single-particle density. Namely, for each orbital, $f_j^\sigma(\mathbf{r})$, we write,

$$f_j^\sigma(\mathbf{r}) = \sum_{\mathbf{k}} a_{\mathbf{k}}^{j,\sigma} \phi_{\mathbf{k}}^\sigma(\mathbf{r}, [n^\sigma]), \quad (32)$$

$$\phi_{\mathbf{k}}^\sigma(\mathbf{r}, [n^\sigma]) = \sqrt{\frac{n^\sigma(\mathbf{r})}{N^\sigma}} \exp\{i \mathbf{k} \cdot \mathbf{R}^\sigma(\mathbf{r}, [n^\sigma])\}, \quad (33)$$

where $\phi_{\mathbf{k}}^\sigma(\mathbf{r}, [n^\sigma])$ are the elements of an orthonormal and complete basis^{25–27}, the *equidensity basis*, where $\mathbf{k} = (k_x, k_y, k_z)$ denote a set of three signed integers, the $a_{\mathbf{k}}^{j,\sigma}$ are expansion coefficients, and the vector $\mathbf{R}^\sigma(\mathbf{r}, [n^\sigma])$ is defined by the expressions,

$$\begin{aligned} R_1^\sigma(x, y, z, [n^\sigma]) &= \frac{2\pi}{N^\sigma(y, z, [n^\sigma])} \int_{-\infty}^x dx' n^\sigma(x', y, z, [n^\sigma]) \\ R_2^\sigma(y, z, [n^\sigma]) &= \frac{2\pi}{N^\sigma(z, [n^\sigma])} \int_{-\infty}^y dy' N^\sigma(y', z, [n^\sigma]) \\ R_3^\sigma(z, [n^\sigma]) &= \frac{2\pi}{N^\sigma[n^\sigma]} \int_{-\infty}^z dz' N^\sigma(z', [n^\sigma]) \end{aligned} \quad (34)$$

with

$$\begin{aligned} N^\sigma(y, z, [n^\sigma]) &= \int_{-\infty}^{\infty} dx' n^\sigma(x', y, z, [n^\sigma]) \\ N^\sigma(z, [n^\sigma]) &= \int_{-\infty}^{\infty} dy' N^\sigma(y', z, [n^\sigma]) \\ N^\sigma[n^\sigma] &= \int_{-\infty}^{\infty} dz' N^\sigma(z', [n^\sigma]) \end{aligned} \quad (35)$$

where $0 \leq R_1, R_2, R_3 \leq 2\pi$. The transformation, $\mathbf{r} \rightarrow \mathbf{R}$, maps three-dimensional coordinate space onto the volume of a cube of side 2π with the points at infinity mapped onto the surface of the volume. Note that the R are explicit functionals of the density. This particular choice of R_1, R_2, R_3 is not unique, with other choices, e.g. permuting coordinates or other coordinate systems, being possible²⁸ as well. In the following we use the definitions given in equations (34) and (35).

The coefficients, $a_{\mathbf{k}}^{j,\sigma}$, are given as the overlap integrals,

$$a_{\mathbf{k}}^{j,\sigma} = \int f_j^\sigma(\mathbf{r}) \phi_{\mathbf{k}}^{\sigma*}(\mathbf{r}, [n]) d\mathbf{r}. \quad (36)$$

The functional derivative of the Coulomb energy can now be carried out through the differentiation of the orbitals under the

integral sign in Eq. (29). The procedure is as follows: We replace the orbitals in the exchange term with their expansions in terms of the equidensity basis, and use the property of functional derivatives,

$$\frac{\delta n^{\sigma''}(\mathbf{r}')}{\delta n^\sigma(\mathbf{r})} = \delta_{\sigma,\sigma''} \delta(\mathbf{r} - \mathbf{r}'), \quad (37)$$

to perform the functional differentiation of the exchange term. It is clear that any density can be used to construct the equidensity basis, and the corresponding expansion of the KS orbitals. However, only the density corresponding to the KS orbitals is useful to construct the equidensity basis. This choice allows a direct functional differentiation of the basis with respect to the density at each iteration step.

A. Coulomb Potential Calculation

In general, the Coulomb potential is given by the functional derivative of the Coulomb energy with respect to the density,

$$\begin{aligned} v^{(U)}(\mathbf{r}') &= \frac{\delta}{\delta n(\mathbf{r}')} \left(\frac{1}{2} \int \int d\mathbf{r}_1 d\mathbf{r}_2 U(\mathbf{r}_1, \mathbf{r}_2) n_s(\mathbf{r}_1, \mathbf{r}_2) \right) \\ &= \frac{1}{2} \int \int d\mathbf{r}_1 d\mathbf{r}_2 U(\mathbf{r}_1, \mathbf{r}_2) \left[\frac{\delta n_s(\mathbf{r}_1, \mathbf{r}_2)}{\delta n(\mathbf{r}')} \right]. \end{aligned} \quad (38)$$

For three-dimensional systems the interaction U is given by the expression,

$$U(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (39)$$

(where clearly U has no functional dependence on the density).

We split the pair density into two parts, the well known Hartree and the exchange contributions (with i in f_i a compound index that includes spin),

$$\begin{aligned} n_s(\mathbf{r}_1, \mathbf{r}_2) &= \sum_{ij, i \neq j}^N \left[f_i^*(\mathbf{r}_1) f_j^*(\mathbf{r}_2) f_i(\mathbf{r}_1) f_j(\mathbf{r}_2) \right. \\ &\quad \left. - f_i^*(\mathbf{r}_1) f_j^*(\mathbf{r}_2) f_j(\mathbf{r}_1) f_i(\mathbf{r}_2) \delta_{\sigma_i, \sigma_j} \right] \end{aligned} \quad (40)$$

$$\begin{aligned} &= n(\mathbf{r}_1) n(\mathbf{r}_2) \\ &\quad - \sum_{ij}^N \left[f_i^*(\mathbf{r}_1) f_j^*(\mathbf{r}_2) f_j(\mathbf{r}_1) f_i(\mathbf{r}_2) \delta_{\sigma_i, \sigma_j} \right] \end{aligned} \quad (41)$$

$$= n(\mathbf{r}_1) n(\mathbf{r}_2) + J_s(\mathbf{r}_1, \mathbf{r}_2) \quad (42)$$

where the exchange term has contributions from likewise spins only. In this form, the sum runs over all i and j . Since the potential from the Hartree contribution is trivial, in the following we concentrate on the functional derivative of the exchange term, $J_s(\mathbf{r}_1, \mathbf{r}_2)$.

Applying the product rule of functional differentiation yields the expression

$$\begin{aligned}
v_x^\sigma &= \frac{\delta J_s(\mathbf{r}_1, \mathbf{r}_2)}{\delta n^\sigma(\mathbf{r}')} \\
&= - \sum_{ij}^N \left[\delta_{\sigma_i, \sigma_j, \sigma} \left\{ \right. \right. \\
&\quad + \frac{\delta f_i^*(\mathbf{r}_1)}{\delta n^\sigma(\mathbf{r}')} f_j^*(\mathbf{r}_2) f_j(\mathbf{r}_1) f_i(\mathbf{r}_2) \\
&\quad + f_i^*(\mathbf{r}_1) \frac{\delta f_j^*(\mathbf{r}_2)}{\delta n^\sigma(\mathbf{r}')} f_j(\mathbf{r}_1) f_i(\mathbf{r}_2) \\
&\quad + f_i^*(\mathbf{r}_1) f_j^*(\mathbf{r}_2) \frac{\delta f_j(\mathbf{r}_1)}{\delta n^\sigma(\mathbf{r}')} f_i(\mathbf{r}_2) \\
&\quad \left. \left. + f_i^*(\mathbf{r}_1) f_j^*(\mathbf{r}_2) f_j(\mathbf{r}_1) \frac{\delta f_i(\mathbf{r}_2)}{\delta n^\sigma(\mathbf{r}')} \right\} \right]. \quad (43)
\end{aligned}$$

In general, the integrals obtained combining (38), (42) and (43) have the form (U is symmetric in \mathbf{r}_1 and \mathbf{r}_2),

$$\int \int d\mathbf{r}_1 d\mathbf{r}_2 U(\mathbf{r}_1, \mathbf{r}_2) f_a^*(\mathbf{r}_2) f_b^*(\mathbf{r}_1) f_c(\mathbf{r}_2) \frac{\delta f_d(\mathbf{r}_1)}{\delta n(\mathbf{r}')} , \quad (44)$$

where $a, b, c, d \in \{i, j\}$. We define the integral I^{ij} :

$$I^{ij}(\mathbf{r}_1) := \int d\mathbf{r}_2 U(\mathbf{r}_1, \mathbf{r}_2) f_i^*(\mathbf{r}_2) f_j(\mathbf{r}_2), \quad (45)$$

that is known to be smooth. The detailed evaluation of these integrals for three-dimensional systems is given in Appendix A.

Since U is symmetric in the spatial coordinates and $I^{ij} = (I^{ji})^*$ equation (43) can be further simplified. We use the fact that \mathbf{r}_1 and \mathbf{r}_2 as well as the summation indices i and j can be interchanged, to obtain the expression,

$$\begin{aligned}
v_x^\sigma(\mathbf{r}') &= \frac{1}{2} \int \int d\mathbf{r}_1 d\mathbf{r}_2 U(\mathbf{r}_1, \mathbf{r}_2) \frac{\delta J_s(\mathbf{r}_1, \mathbf{r}_2)}{\delta n^\sigma(\mathbf{r}')} \\
&= - \sum_{ij}^N \left[\delta_{\sigma_i, \sigma_j, \sigma} \left\{ \int d\mathbf{r} I^{ij}(\mathbf{r}) f_j(\mathbf{r}) \frac{\delta f_i^*(\mathbf{r})}{\delta n^\sigma(\mathbf{r}')} \right. \right. \\
&\quad \left. \left. + \int d\mathbf{r} I^{ij}(\mathbf{r}) f_j^*(\mathbf{r}) \frac{\delta f_i(\mathbf{r})}{\delta n^\sigma(\mathbf{r}')} \right\} \right], \quad (46)
\end{aligned}$$

or

$$v_x^\sigma(\mathbf{r}') = -2\Re \sum_{ij}^N \delta_{\sigma_i, \sigma_j, \sigma} \int d\mathbf{r} I^{ij}(\mathbf{r}) f_j^*(\mathbf{r}) \frac{\delta f_i(\mathbf{r})}{\delta n^\sigma(\mathbf{r}')}, \quad (47)$$

where $\delta_{\sigma_i, \sigma_j, \sigma}$ equals 1 when $\sigma_i = \sigma_j = \sigma$ and vanishes otherwise. The exchange potential is always real. It becomes clear that the crucial quantity of interest is the derivative of an orbital with respect to the density, $\frac{\delta f(\mathbf{r})}{\delta n(\mathbf{r}')}.$

B. Explicit Derivatives of Orbitals

Within SIF, the derivative of an orbital with respect to the density is straightforward. Using the expansion (32) and the

definition of the equidensity basis (33) we obtain the expression,

$$\begin{aligned}
\frac{\delta f_i^{\sigma_i}(\mathbf{r})}{\delta n^\sigma(\mathbf{r}')} &= \sum_{\mathbf{k}} \frac{\delta}{\delta n^\sigma(\mathbf{r}')} a_{\mathbf{k}}^{i, \sigma_i} \phi_{\mathbf{k}}^{\sigma_i}(\mathbf{r}, [n^{\sigma_i}]) \\
&= \sum_{\mathbf{k}} \left[\frac{1}{\sqrt{N^{\sigma_i}}} a_{\mathbf{k}}^{i, \sigma_i} e^{i\mathbf{k} \cdot \mathbf{R}} \frac{\delta \sqrt{n^{\sigma_i}(\mathbf{r})}}{\delta n^\sigma(\mathbf{r}')} \right. \\
&\quad + \sqrt{n^{\sigma_i}(\mathbf{r})} a_{\mathbf{k}}^{i, \sigma_i} e^{i\mathbf{k} \cdot \mathbf{R}} \frac{\delta \frac{1}{\sqrt{N^{\sigma_i}}}}{\delta n^\sigma(\mathbf{r}')} \\
&\quad + \sqrt{\frac{n^{\sigma_i}(\mathbf{r})}{N^{\sigma_i}}} i a_{\mathbf{k}}^{i, \sigma_i} e^{i\mathbf{k} \cdot \mathbf{R}} \mathbf{k} \cdot \frac{\delta R(\mathbf{r}, [n^{\sigma_i}])}{\delta n^\sigma(\mathbf{r}')} \\
&\quad \left. + \frac{\delta a_{\mathbf{k}}^{i, \sigma_i}}{\delta n^\sigma(\mathbf{r}')} \phi_{\mathbf{k}}^{\sigma_i}(\mathbf{r}, [n^{\sigma_i}]) \right] \quad (48)
\end{aligned}$$

$$\begin{aligned}
\frac{\delta f_i^{\sigma_i}(\mathbf{r})}{\delta n^\sigma(\mathbf{r}')} &= \sum_{\mathbf{k}} \left[\delta_{\sigma, \sigma_i} \frac{\delta(\mathbf{r} - \mathbf{r}')}{2n^{\sigma_i}(\mathbf{r})} a_{\mathbf{k}}^{i, \sigma_i} \phi_{\mathbf{k}}^{\sigma_i}(\mathbf{r}) \right. \\
&\quad + \delta_{\sigma, \sigma_i} \sqrt{n^{\sigma_i}(\mathbf{r})} a_{\mathbf{k}}^{i, \sigma_i} e^{i\mathbf{k} \cdot \mathbf{R}} \left(-\frac{1}{2(N^{\sigma_i})^{3/2}} \right) \\
&\quad + i a_{\mathbf{k}}^{i, \sigma_i} \phi_{\mathbf{k}}^{\sigma_i}(\mathbf{r}, [n^{\sigma_i}]) \mathbf{k} \cdot \frac{\delta R(\mathbf{r}, [n^{\sigma_i}])}{\delta n^\sigma(\mathbf{r}')} \\
&\quad \left. + \frac{\delta a_{\mathbf{k}}^{i, \sigma_i}}{\delta n^\sigma(\mathbf{r}')} \phi_{\mathbf{k}}^{\sigma_i}(\mathbf{r}, [n^{\sigma_i}]) \right]
\end{aligned}$$

$$\begin{aligned}
\frac{\delta f_i^{\sigma_i}(\mathbf{r})}{\delta n^\sigma(\mathbf{r}')} &= \delta_{\sigma, \sigma_i} \frac{\delta(\mathbf{r} - \mathbf{r}')}{2n^{\sigma_i}(\mathbf{r})} f_i^{\sigma_i}(\mathbf{r}) - \delta_{\sigma, \sigma_i} \frac{f_i^{\sigma_i}}{2N^{\sigma_i}} \\
&\quad + \sum_{\mathbf{k}} \left[i a_{\mathbf{k}}^{i, \sigma_i} \phi_{\mathbf{k}}^{\sigma_i}(\mathbf{r}, [n^{\sigma_i}]) \mathbf{k} \cdot \frac{\delta R(\mathbf{r}, [n^{\sigma_i}])}{\delta n^\sigma(\mathbf{r}')} \right. \\
&\quad \left. + \frac{\delta a_{\mathbf{k}}^{i, \sigma_i}}{\delta n^\sigma(\mathbf{r}')} \phi_{\mathbf{k}}^{\sigma_i}(\mathbf{r}, [n^{\sigma_i}]) \right]. \quad (49)
\end{aligned}$$

For the sake of formal completeness, we include the functional derivative of the normalization integrals N^σ with respect to the density, that leads to the second term after the last equals sign.

When the spin of the orbital and the spin of the density with respect to which it is differentiated coincide, the last expression reduces to the form,

$$\begin{aligned}
\frac{\delta f_i^\sigma(\mathbf{r})}{\delta n^\sigma(\mathbf{r}')} &= \frac{\delta(\mathbf{r} - \mathbf{r}')}{2n^\sigma(\mathbf{r})} f_i^\sigma(\mathbf{r}) - \frac{f_i^\sigma(\mathbf{r})}{2N^\sigma} \\
&\quad + \frac{\delta R(\mathbf{r}, [n^\sigma])}{\delta n^\sigma(\mathbf{r}')} \cdot \sum_{\mathbf{k}} i \mathbf{k} a_{\mathbf{k}}^{i, \sigma} \phi_{\mathbf{k}}^\sigma(\mathbf{r}, [n^\sigma]) \\
&\quad + \sum_{\mathbf{k}} \frac{\delta a_{\mathbf{k}}^{i, \sigma}}{\delta n^\sigma(\mathbf{r}')} \phi_{\mathbf{k}}^\sigma(\mathbf{r}, [n^\sigma]), \quad (50)
\end{aligned}$$

where the second term (from the derivative of the normalization) leads to a constant shift in the potential and can be neglected. In the following we also neglect the last term containing the functional derivative of the expansion coefficients

with respect to the density. The reason for making this seeming approximation will be discussed in other work.

The third term of Eq. (50) involves an infinite sum over \mathbf{k} , raising questions about convergence. This problem is circumvented through the realization that the same infinite sum occurs in the gradients of the orbitals. As shown in Appendix C, comparing functional and spatial derivatives allows the replacement of the sum over \mathbf{k} with expressions involving partial derivatives of the orbitals. For example, as shown there, in the one-dimensional case we obtain the result,

$$\begin{aligned} \sum_k a_k^\sigma i k \phi_k^\sigma(x) &= \frac{N^\sigma}{2\pi n^\sigma(x)} \left[f' - \frac{1}{2n^\sigma(x)} f(x) n^{\sigma'} \right] \\ &= \frac{N^\sigma}{2\pi} \frac{1}{\sqrt{n^\sigma(x)}} \left(\frac{f(x)}{\sqrt{n^\sigma(x)}} \right)', \end{aligned} \quad (51)$$

where primes on functions denote spatial derivatives. The three-dimensional case follows analogously, leading to the expression,

$$\begin{aligned} \sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(i\mathbf{k}) &=: \begin{pmatrix} Q_x^\sigma \\ Q_y^\sigma \\ Q_z^\sigma \end{pmatrix} = \mathbf{Q}^\sigma = \\ &\begin{pmatrix} \frac{N^\sigma(y,z)}{2\pi n^\sigma(\mathbf{r})} \left[\nabla_x f - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial x} \right] \\ \frac{N^\sigma(z)}{2\pi N^\sigma(y,z)} \left[\nabla_y f - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial y} - Q_x^\sigma \beta_{12}^\sigma \right] \\ \frac{N^\sigma}{2\pi N^\sigma(z)} \left[\nabla_z f - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial z} - Q_x^\sigma \beta_{13}^\sigma - Q_y^\sigma \beta_{23}^\sigma \right] \end{pmatrix}, \end{aligned} \quad (52)$$

with β_{ab} being the partial derivatives of \mathbf{R} with respect to the coordinates,

$$\beta_{ab} := \frac{\partial R_a}{\partial b} \quad a, b \in \{x, y, z\}, \quad (53)$$

given for the three-dimensional case in Appendix B 1.

In short, we can write

$$\begin{aligned} \frac{\delta f_i^\sigma(\mathbf{r})}{\delta n^\sigma(\mathbf{r}')} &= \frac{\delta(\mathbf{r} - \mathbf{r}')}{2n^\sigma(\mathbf{r})} f_i^\sigma(\mathbf{r}) - \frac{f_i^\sigma}{2N^\sigma} \\ &\quad + \frac{\delta \mathbf{R}(\mathbf{r}, [n^\sigma])}{\delta n(\mathbf{r}')} \cdot \mathbf{Q}^\sigma, \end{aligned} \quad (54)$$

where the \mathbf{Q} include summations over \mathbf{k} to infinite order.

Still to be considered is the functional derivative of \mathbf{R} with respect to the density. The derivation is shown in detail in Appendix B 2. For the one-dimensional case we obtain the expression,

$$\frac{\delta R_1(x, [n^\sigma])}{\delta n^\sigma(x')} = \frac{2\pi}{N^\sigma} \Theta(x - x') \quad (55)$$

while in three-dimensions we find

$$\frac{\partial R_1(x, y, z, [n^\sigma])}{\partial n^\sigma(\mathbf{r}'')} = \frac{\delta(y - y'') \delta(z - z'')}{N^\sigma(y, z)} \times$$

$$\begin{aligned} &\begin{bmatrix} 2\pi \Theta(x - x'') - R_1^\sigma(x, y, z) \end{bmatrix} \\ \frac{\partial R_2(y, z, [n^\sigma])}{\partial n^\sigma(\mathbf{r}'')} &= \frac{\delta(z - z'')}{N^\sigma(z)} \times \\ &\begin{bmatrix} 2\pi \Theta(y - y'') - R_2^\sigma(y, z) \end{bmatrix} \\ \frac{\partial R_3(z, [n^\sigma])}{\partial n^\sigma(\mathbf{r}'')} &= \frac{1}{N^\sigma} \begin{bmatrix} 2\pi \Theta(z - z'') - R_3^\sigma(z) \end{bmatrix}. \end{aligned} \quad (56)$$

We have now derived an analytic and closed-form expression for the functional derivative of an orbital with respect to the density. Through the use of the product rule, these expressions can be used to obtain the contribution, $v_x(\mathbf{r})$, to the Coulomb potential. Computational details and the final expressions for the three-dimensional case are given in Appendix D.

Before closing this section it should be noted that our results for the exchange energies and potentials neglecting of the last term in Eq. (50) match those of Harbola and Sahní²⁹, as discussed later in Section V C, which are obtained from electrostatics, through a method that is exact for spherical charges and independent of an expansion in an orthonormal basis.

C. Formal Summary

We summarize the discussion of the previous section. The use of spatial derivatives allows us to eliminate the explicit evaluation of the equidensity basis and the expansion coefficients, leading to a closed-form expression for the functional derivative of an orbital with respect to the density. In the one-dimensional case we obtain the expression,

$$\begin{aligned} \frac{\delta f^\sigma(x)}{\delta n^\sigma(x'')} &= \frac{f^\sigma(x)}{2n^\sigma(x)} \delta(x - x'') - \frac{f^\sigma(x)}{2N^\sigma} \\ &\quad + \left(\frac{1}{n^\sigma(x)} \left[f^{\sigma'}(x) - \frac{f^\sigma(x) n^{\sigma'}(x)}{2n^\sigma(x)} \right] \right) \Theta(x - x''). \end{aligned} \quad (57)$$

The analogous results in three-dimensions take the form,

$$\begin{aligned} \frac{\delta f^\sigma(\mathbf{r})}{\delta n^\sigma(\mathbf{r}'')} &= \frac{f^\sigma(\mathbf{r})}{2n^\sigma(\mathbf{r})} \delta(\mathbf{r} - \mathbf{r}'') - \frac{f^\sigma(\mathbf{r})}{2N^\sigma} \\ &\quad + \frac{Q_x^\sigma(\mathbf{r})}{N^\sigma(y, z)} [2\pi \Theta(x - x'') - R_1^\sigma(x, y, z)] \\ &\quad \delta(y - y'') \delta(z - z'') \\ &\quad + \frac{Q_y^\sigma(\mathbf{r})}{N^\sigma(z)} [2\pi \Theta(y - y'') - R_2^\sigma(y, z)] \\ &\quad \delta(z - z'') \\ &\quad + \frac{Q_z^\sigma(\mathbf{r})}{N^\sigma} [2\pi \Theta(z - z'') - R_3^\sigma(z)], \end{aligned} \quad (58)$$

with the quantities R defined in (34), the N in (35) and the \mathbf{Q} in (52). Computational details are given in Appendix D. The calculation of the potential becomes now straightforward using equations (47) and (45).

D. Iterative Procedure

The solution of the KS equations relies on an iterative procedure, with an updated KS potential and density determined at each iteration step. The sequence of steps in the treatment of the KS equations is summarized below:

1. At each step, i , of the iteration, determine the orbitals, $f_j^{(i)}(\mathbf{r})$, and the density, $n^{(i)}(\mathbf{r})$.
2. Determine the derivatives of the orbitals with the respect to the density, take the functional derivative of the Coulomb energy with respect to the density in terms of spatial gradients, and obtain the Coulomb energy contribution to the KS potential.
3. Solve the KS equation for the new potential, go back to the first step and iterate until convergence is reached within some preset tolerance.

In short, the only difference with conventional procedures is the treatment of the full Coulomb potential expressed in terms of the pair density, rather than just the Hartree term or modifications to it.

IV. EXAMPLES

In this section we present the results of applications of our method to two systems for which the exact answers are known analytically, to a one dimensional model system, and finally on the series of atomic systems from Helium to Krypton. For the latter case, we compare our results to those from HF and OEP methods and discuss the differences between the results of the three approaches.

A. Analytic Examples

The formalism allows the expression of the functional derivatives of the exchange energy with respect to the density by analytic means and leads to closed-form expressions in terms of the spatial gradients of the orbital functions. These expressions can be compared to exact results in cases where analytic expressions are known.

1. Two-Electron Systems

As a first example we discuss the ground state of a two-electron systems, such as the Helium atom or the Hydrogen dimer (H_2), with two electrons of opposite spin in the same spatial orbital under the same external potential.

Assuming real, and node free orbitals we obtain

$$n^\sigma(\mathbf{r}) = \sum_{i=1}^1 |f_i(\mathbf{r})|^2 = |f(\mathbf{r})|^2 \quad (60)$$

$$f(\mathbf{r}) = \sqrt{n^\sigma(\mathbf{r})} \quad (61)$$

$$\frac{\delta f(\mathbf{r})}{\delta n^\sigma(\mathbf{r}')} = \frac{1}{2\sqrt{n^\sigma(\mathbf{r})}} \delta(\mathbf{r} - \mathbf{r}') \quad (62)$$

$$f \frac{\delta f}{\delta n^\sigma} = \frac{1}{2} \delta(\mathbf{r} - \mathbf{r}'), \quad (63)$$

from which the exchange potential can be determined as follows:

$$v_x^\sigma(\mathbf{r}) = \frac{1}{2} \int \int d\mathbf{r}_1 d\mathbf{r}_2 U(\mathbf{r}_1, \mathbf{r}_2) \frac{\delta J_s(\mathbf{r}_1, \mathbf{r}_2)}{\delta n^\sigma(\mathbf{r})} \quad (64)$$

$$= - \int \int d\mathbf{r}_1 d\mathbf{r}_2 U(\mathbf{r}_1, \mathbf{r}_2) \left\{ f(\mathbf{r}_1) \frac{\delta f(\mathbf{r}_1)}{\delta n^\sigma} f(\mathbf{r}_2) f(\mathbf{r}_2) + f(\mathbf{r}_2) \frac{\delta f(\mathbf{r}_2)}{\delta n^\sigma} f(\mathbf{r}_1) f(\mathbf{r}_1) \right\} \quad (65)$$

$$= - \int \int d\mathbf{r}_1 d\mathbf{r}_2 U(\mathbf{r}_1, \mathbf{r}_2) \left\{ \frac{1}{2} \delta(\mathbf{r} - \mathbf{r}_1) f(\mathbf{r}_2) f(\mathbf{r}_2) + \frac{1}{2} \delta(\mathbf{r} - \mathbf{r}_2) f(\mathbf{r}_1) f(\mathbf{r}_1) \right\} \quad (66)$$

$$= - \int d\mathbf{r}_1 U(\mathbf{r}_1, \mathbf{r}) n^\sigma(\mathbf{r}_1)$$

$$v_x^\sigma(\mathbf{r}) = -\frac{1}{2} \int d\mathbf{r}_1 U(\mathbf{r}_1, \mathbf{r}) n(\mathbf{r}_1) = -\frac{1}{2} V^{\text{Hartree}}(\mathbf{r}). \quad (67)$$

The exchange potential is exactly half of the Hartree potential but with the opposite sign, so that the self-interaction error is half of the Hartree term.

Using the method proposed in this paper, we write

$$f(\mathbf{r}) = \sum_{\mathbf{k}=0} a_{\mathbf{k}} \phi_{\mathbf{k}}(\mathbf{r}) \quad \text{with} \quad a_0 = 1, \quad (68)$$

where all coefficients other than $\mathbf{k} = \mathbf{0}$ vanish. From Eq. (50) we obtain the expression,

$$\frac{\delta f(\mathbf{r})}{\delta n^\sigma(\mathbf{r}')} = \frac{\delta(\mathbf{r} - \mathbf{r}')}{2n^\sigma(\mathbf{r})} f(\mathbf{r}) = \frac{\delta(\mathbf{r} - \mathbf{r}')}{2f(\mathbf{r})}. \quad (69)$$

Using Eq. (47) for the exchange potential yields the result,

$$v_x^\sigma(\mathbf{r}') = -2 \int d\mathbf{r} I^{11}(\mathbf{r}) f(\mathbf{r}) \frac{\delta f(\mathbf{r})}{\delta n^\sigma(\mathbf{r}')} \quad (70)$$

$$= -I^{11}(\mathbf{r}') = - \int d\mathbf{r} U(\mathbf{r}, \mathbf{r}') f(\mathbf{r}) f(\mathbf{r}) \quad (71)$$

$$= - \int d\mathbf{r} U(\mathbf{r}, \mathbf{r}') n^\sigma(\mathbf{r}) \quad (72)$$

$$v_x^\sigma(\mathbf{r}') = -\frac{1}{2} \int d\mathbf{r} U(\mathbf{r}, \mathbf{r}') n(\mathbf{r}) = -\frac{1}{2} V^{\text{Hartree}}(\mathbf{r}') \quad (73)$$

For this simple example, the SIF method reproduces the correct analytic expression for the exchange potential.

2. Hartree Potential

Our second example deals with the Hartree term. The functional derivative of the Hartree energy E^H with respect to the density is well known. From

$$E^H = \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (74)$$

we obtain

$$\frac{\delta E^H}{\delta n(\mathbf{r}'')} = V^H(\mathbf{r}'') = \int d\mathbf{r} \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}''|}. \quad (75)$$

It can also be shown, that

$$\frac{\delta E^H}{\delta n(\mathbf{r}'')} = \frac{\delta E^H}{\delta n^\uparrow(\mathbf{r}'')} = \frac{\delta E^H}{\delta n^\downarrow(\mathbf{r}'')} = V^H(\mathbf{r}''). \quad (76)$$

We now express the density in terms of orbitals,

$$n^\sigma(\mathbf{r}) = \sum_{i=1}^{N^\sigma} f_i^*(\mathbf{r}) f_i(\mathbf{r}), \quad (77)$$

and express the orbitals in terms of the equidensity basis, and take the functional derivative of E^H written in terms of the expanded forms. The results leads to V^H . The detailed derivation of this result is shown in Appendix E.

B. Numerical Examples

In this section we apply our method to one-dimensional systems in terms of the particles-in-a-box problem and to realistic atomic systems.

1. One-dimensional Square Well

The work reported in this section is designed to test a simple case of non-interacting, spinless Fermions confined in an one-dimensional well of length, $L = |x_1 - x_0| = 1$, with infinite potential walls. We choose $N = 6$. This example is used for illustrating the method, deriving the potential corresponding to the energy for a given form of the inter-particle interaction. We restrict ourselves to a non-self consistent solution for a vanishing (or constant) potential. We choose an inter-particle interaction that decays exponentially with respect to inter-particle distance,

$$U(x_1, x_2) = \Lambda e^{-\lambda|x_1 - x_2|}, \quad (78)$$

that allows us the freedom of manipulating the range of the interaction and assess its effects on the exchange potential.

The N lowest in energy orbitals in this case are known analytically and lead to an analytic expression for the density in

Eq. (14) and the pair density, Eq. (42). The normalized wave functions of this system are given by the expressions,

$$f_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad 0 \leq x \leq L, \quad (79)$$

with quantum numbers $n = 1, 2, 3, \dots$. The energies read as

$$E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L}\right)^2, \quad (80)$$

with the ground-state density given by $n(x) = \sum_{n=1}^6 |f_n(x)|^2$.

In analogy to Eq. (34), we define the quantities $R_{1/2/3}(x, y, z)$, that in one dimension reduce³ to a function $q(x)$,

$$q(x) = \frac{2\pi}{N} \int_{x_0}^x n(x') dx'. \quad (81)$$

For the six-electron case, $q(x)$ is shown in Fig. 1. We see that

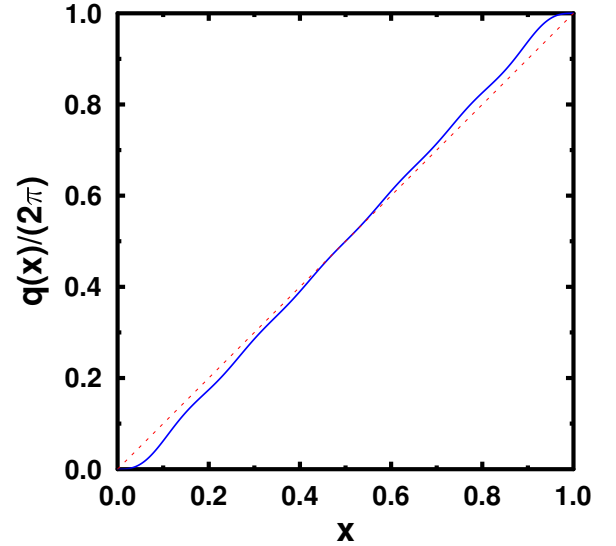


FIG. 1. The quantity $q(x)$ (solid blue line) for the one-dimensional square well example with 6 electrons. The red dashed line shows $q(x) = x$ which corresponds to a constant density. In this case the basis functions ϕ become plane waves.

the function $q(x)$ is almost linear. An exact linear behavior, $q(x) = x$, (red dashed line) would correspond to a constant density with the equidensity orbitals reduced to plane-waves.

The functional derivative of $\frac{\delta q(x)}{\delta n(x'')}$ takes the form,

$$\frac{\delta q(x)}{\delta n(x'')} = \frac{2\pi}{N} \Theta(x - x''). \quad (82)$$

We also have,

$$\frac{\delta f_n(x)}{\delta n(x'')} = \frac{f_n(x)}{n(x)} \delta(x - x'') + \frac{\delta q(x)}{\delta n(x'')} \sum_k a_k^n \phi_k[n(x)].$$

In spite of the dependence on k , the sum on the right-hand side converges sufficiently rapidly to be numerically stable. In this case, the equidensity basis functions, $\phi_k(x)$, take the form,

$$\phi_k(x) = \sqrt{\frac{n(x)}{N}} e^{i k q(x)} = \sqrt{\frac{n(x)}{N}} e^{i k q(x, [n])}. \quad (83)$$

There exist two choices for k in constructing a complete and orthonormal set of basis functions: Either signed whole integer values, $k = 0, \pm 1, \pm 2, \pm 3, \dots$, or half-integer values, $k = \pm \frac{1}{2}, \pm \frac{3}{2}, \pm \frac{5}{2}, \dots$. The rate of convergence of the expansion of the orbitals is found to depend on spatial symmetry, with those even under reflection (symmetric) about the center of the box being described more efficiently by whole integer values of k , while half-integer values lead to faster convergence of the orbitals that are odd under reflection (antisymmetric). A plot of the coefficients vs. values of k is shown in Fig. 2. We find that with the choice of the faster converging

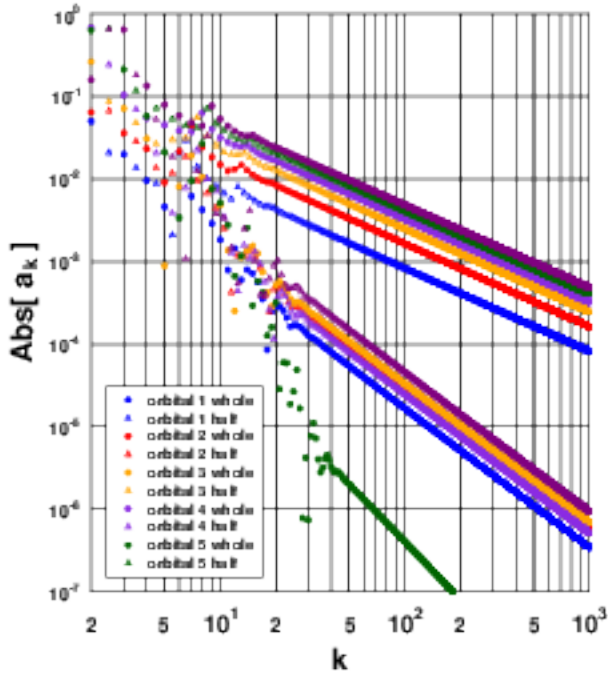


FIG. 2. Log-log plot of expansion coefficients of spatially symmetric (even under reflection) and antisymmetric (odd under reflection) orbitals in terms of an equidensity basis, as indicated in the legend.

expansion the error in the norm becomes smaller than 10^{-5} when more than 100 basis functions are taken into account. Generally, we find that fewer than 1,000 functions are sufficient for convergence.

The ground-state density of the system, (the six electrons occupying the orbitals labeled $n = 1, 2, \dots, 6$), is shown in Fig 3, while the pair density is shown in Fig. 4, with the number of basis functions indicated in the panel. Within the resolution of the figure, the two results are essentially indistinguishable. The same rate of convergence characterizes the pair density, shown in Fig. 4. We note the vanishing of the pair density along the line $x_1 = x_2$, as expected from Eq. (40).

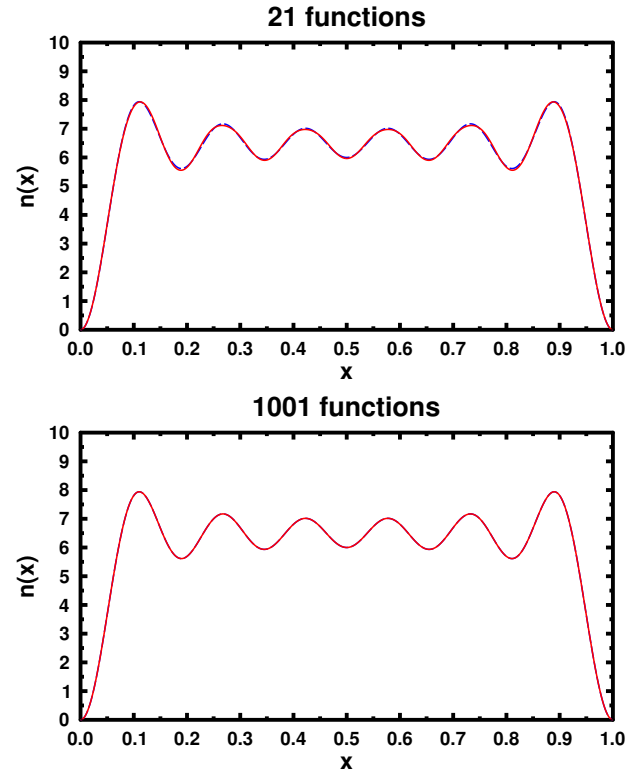


FIG. 3. Ground-state density of six non-interacting electrons in an one-dimensional box with infinite walls as discussed in the text. The blue dashed line marks the analytic expression, plotted below the other curve. At this scale they are almost indistinguishable.

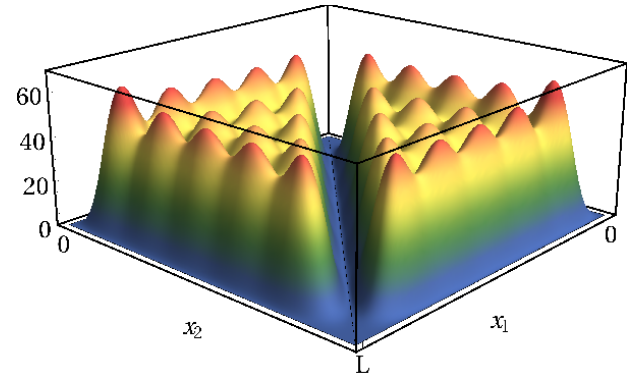


FIG. 4. Non-interacting Ground-state pair density of six non-interacting electrons in an one-dimensional box with infinite walls as discussed in the text.

Another quantity to look at for convergence is the infinite sum over k appearing in Eq. (50). The result with the sums carried out to infinite order is given by the analytic expression in Eq. (51). The sums over k for the first three orbitals are shown in Fig. 5 for different numbers of expansion coefficients and basis functions taken into account, with those used chosen symmetrically around $k = 0$. For this example,

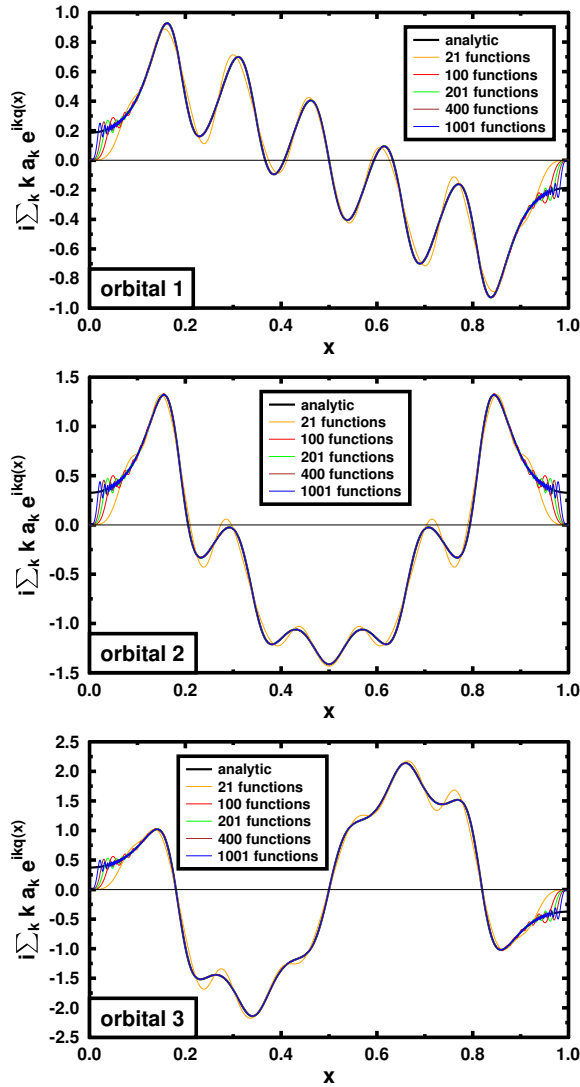


FIG. 5. Infinite sum, see Eq. (51), evaluated for the first three orbitals of the six electron example. Convergence is shown by increasing the numbers of coefficients a_k (chosen symmetrically around 0) in comparison to the analytic result.

we find a rather good agreement using a few tens of coefficients in a broad range in space, between about $x = 0.1$ and $x = 0.9$ in Fig. 5. At the boundaries, the difference between the analytic expression and the truncated sums increases, the oscillations being a manifestation of the Gibbs phenomenon. Even though the results show convergence with the number of terms taken into account, we use the closed-form expressions of Eq. (51). This bypasses the explicit construction of the equidensity basis and the expansion coefficients.

Fig. 6 shows the potential obtained for the four values of $\lambda = 1, 10, 50, 100$, as defined in (78), using both the Hartree expression (blue dashed curves) for the interaction energy, Eq. (23), as well as the quantum mechanically correct expression, Eq. (24) (red solid line). In all cases, convergence is well established with about 200 basis functions, although the

results shown here correspond to 1,000 terms taken into account. The analytic expressions lead to the same result. An

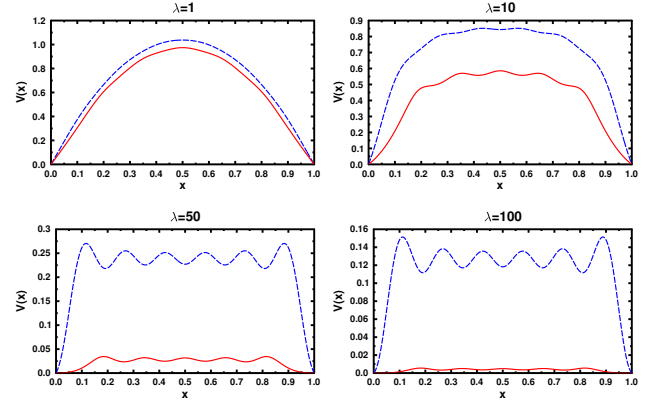


FIG. 6. Single-particle potential contributed by the interaction energy in the system of six non-interacting electrons confined in a box with infinite walls as discussed in the text. The blue dashed line is calculated from Eq. (23) (Hartree), whereas the red solid line is based on Eq. (24) (pair density).

immediate effect of the quantum expression are the lower values of the potential obtained from Eq. (24), caused by the presence of the exchange term that reduces the effective region of interaction of two electrons. Of interest is also the behavior of the two different expressions for the potential in the limit of short-range interaction, or large values of λ . The Hartree term yields a potential that approaches the form of the density, essentially reaching that form for $\lambda = 100$ (upper curve in panel on lower right-hand corner). In that limit, the interaction potential resembles a delta-function in two-particle space and the energy given by the Hartree term is simply proportional to the density at the point $x_1 = x_2$.

The behavior is considerably different when the pair density is used to calculate the interaction energy. Now, in the limit of short-range interaction, and spinless fermions, two particles cease interacting altogether because the pair density vanishes in the region in which the interaction is noticeably non-zero and the contribution to the single-particle potential drops essentially to zero (lower curve in panel in lower right-hand corner in the figure).

2. Atomic Calculations

In the following we apply the SIF method to realistic atomic systems. Details of the calculations, in particular of the evaluation of the Coulomb and exchange potential are given in Appendix D. Because the form of the correlation energy is currently unknown, the results presented are all fully self-consistent and converged within the exchange-only mode ($E_c = 0$). This allows us to compare SIF results with those obtained within the exchange-only OEP and the HF methods.

Fig. 7 show the results for Helium, Lithium, Beryllium, Boron, Neon and Argon obtained from a self-consistent

exchange-only calculation. The left column shows the exchange potential on a logarithmic scale that allows a detailed study of the behavior close to the nucleus. To emphasize the asymptotic behavior, in the middle panel, the same exchange potential is shown on a linear scale, but multiplied by the distance to the nucleus, r . Finally, the density is plotted in the right column. For all examples, the corresponding full OEP results are shown for comparison. Lithium and Boron are spin-polarized, resulting in different potentials for the majority and minority spin channel.

For Helium, the exchange potential within SIF coincides with the one obtained by the OEP method, and therefore the densities are also identical. This identity is not preserved for heavier atoms. As seen in Fig. 7, the SIF potential has always a non-negative slope, whereas the OEP potentials exhibits regions where the slope becomes negative. In the OEP literature⁷ this is referred to as the intershell structure. In Section V, we provide a formal explanation of this behavior.

Even though the potentials are different, the SIF and OEP densities are indistinguishable at the scale of the plot. All exchange potentials behave regularly near the origin, and have an $-1/r$ asymptotic behavior, as expected. For illustrative purposes, we plot the exchange potentials for the atoms Helium to Krypton in Fig. 8.

Total energies for the atom series obtained in SIF, OEP and HF are compared with experiment in Table I and are plotted as difference to experiment in Fig. 9. Experimental data for the total energy can be obtained by summing all ionization potentials of the corresponding atom, a process whose difficulty increases prohibitively with atomic number, Z . Published results for the total energy are often characterized by a number of corrections to account for zero-point motion and relativistic effects. The resulting rather unclear situation for the total energies is discussed in Appendix F. In any case, the experimental values of the ground-state energies lie the lowest compared with those of HF, OEP and SIF in corresponding increasing order. We discuss this order in more detail in the following section.

V. DIFFERENCES BETWEEN HF, OEP AND THE SIF METHODS

A. Comparison with Hartree-Fock

It has become customary in the literature to compare the results of an exchange-only implementation of DFT to those of the HF method, and we follow this practice.

The HF method relies on the direct calculation of a determinantal wave function to minimize the energy of an interacting system. The single-particle orbitals defining the determinant are the basic variables of the method, and their unrestricted variation provides a path to the lowest energy obtained in this procedure. The method, however, does not provide a path to the determination of the ground state of an interacting system.

By contrast, the basic variable in DFT is the density, and the KS orbitals are restricted to those that lead to the density in terms of a non-interacting collection of electrons in an ef-

fective potential, $v_s(\mathbf{r})$. In order to minimize the energy the functional derivative with respect to the density is taken, and evaluated at that particular density formed by the KS orbitals. In an exchange-only implementation of the theory, the restriction of the orbitals to reproduce the density is expected to lead to higher values of the total energy compared with those of the HF method. This, indeed, is the case in all calculations reported here, see Table I. The restrictions can also be discussed in terms of the potential. Within the KS scheme, the potential, see Eq. (20), is local, as in HF the potential becomes orbital-dependent and non-local.

B. Comparison with OEP

Since the most widely used method for obtaining a potential from an energy functional written explicitly in terms of the orbitals is the OEP, we compare our results with the ones obtained in that method. Unfortunately, published results, e.g. for atomic systems, obtained by the OEP method are not conclusive. There are at least two different approaches in implementations of the OEP. The first one is based on the original work by Talman and Shadwick¹⁵, where the susceptibility is approximated by first order perturbation theory and then inverted.

A different approach was suggested by Wu and Yang^{12,19} where the potential is expanded in a basis and the expansion coefficients are varied in attempting to reach convergence. In principle, both approaches should determine the OEP potential and energies uniquely. The uniqueness of the OEP results has been discussed in more detail in the literature^{33,34}. Numerically, however, the two approaches seem to differ as indicated in Fig. 10 showing the exchange potential for Ar determined by four different methods. Heaton-Burgess, Bulat, and Yang³⁵ examined in great detail the numerical convergence of their method and concluded that the oscillatory behavior in the exchange potential (around $r = 10^{-1}$ and 1 in the curve marked OEP), referred to as the *inter-shell structure*, is unphysical. The same interpretation of the inter-shell structure as unphysical has been proposed by Harbola and Sahni (see below).

In their study, Heaton-Burgess et al.³⁵, found that the amplitude of oscillations is related to the finite basis set, or in other words, the oscillations are the result of an unconverged treatment. For Argon, their converged exchange potential is similar to SIF, and does not show any of the so-called inter-shell structure, characterizing the results based on the conventional treatment¹⁵, where the functional derivative of an orbital with respect to the potential is treated within first-order perturbation theory.

The relative order of the energies obtained in HF, OEP and the SIF methodologies can be understood in terms of the variational constraints characterizing each of the methods. As mentioned above, the unrestricted HF method (in the absence of a correlation-energy functional) yields the lowest energies, while the variation of the wave function (KS orbitals) restricted to reproduce the density yields the highest. The OEP method employs a local potential (hence gives energies higher than HF) but allows variations in terms of the orbitals treated

Z	Symbol	Element	EXP ^(a)	EXP ^(b) (Ref. ³⁰)	x-SIF	x-OEP (Ref. ³¹)	HF (Ref. ³¹)
2	He	Helium	-2.90339	-2.904	-2.862	-2.862	-2.862
3	Li	Lithium	-7.47798	-7.47806	-7.432	-7.433	-7.433
4	Be	Beryllium	-14.6685	-14.66736	-14.571	-14.572	-14.573
5	B	Boron	-24.6582	-24.65391	-24.527	-24.528	-24.529
6	C	Carbon	-37.8557±0.0002	-37.8450	-37.687	-37.689	-37.690
7	N	Nitrogen	-54.6119	-54.5892	-54.401	-54.403	-54.405
8	O	Oxygen	-75.1100±0.0001	-75.0673	-74.809	-74.812	-74.814
9	F	Fluorine	-99.8062±0.0001	-99.7339	-99.406	-99.409	-99.411
10	Ne	Neon	-129.0507±0.0059	-128.9376	-128.542	-128.545	-128.547
11	Na	Sodium	-162.4283±0.0032	-162.2546	-161.852	-161.857	-161.859
12	Mg	Magnesium	-200.3100±0.0033	-200.053	-199.606	-199.612	-199.615
13	Al	Aluminum	-242.7121±0.0037	-242.346	-241.868	-241.873	-241.877
14	Si	Silicon	-289.8683±0.0037	-289.359	-288.845	-288.851	-288.854
15	P	Phosphorus	-341.9464±0.0087	-341.259	-340.709	-340.715	-340.719
16	S	Sulfur	-399.0351±0.0050	-398.110	-397.495	-397.502	-397.506
17	Cl	Chlorine	-461.3813±0.0051	-460.148	-459.470	-459.478	-459.483
18	Ar	Argon	-529.1122±0.0093	-527.540	-526.804	-526.812	-526.817
19	K	Potassium	-601.9677±0.0515		-599.150	-599.159	-599.165
20	Ca	Calcium	-680.1022±0.0679		-676.743	-676.752	-676.758
21	Sc	Scandium			-759.718	-759.728	-759.736
22	Ti	Titanium			-848.375	-848.397	-848.407
23	V	Vanadium			-942.852	-942.876	-942.886
24	Cr	Chromium			-1043.334	-1043.350	-1043.360
25	Mn	Manganese			-1149.848	-1149.860	-1149.870
26	Fe	Iron			-1262.425	-1262.440	-1262.450
27	Co	Cobalt			-1381.376	-1381.410	-1381.420
28	Ni	Nickel			-1506.828	-1506.860	-1506.870
29	Cu	Copper			-1638.938	-1638.950	-1638.960
30	Zn	Zinc			-1777.820	-1777.830	-1777.850
31	Ga	Gallium			-1923.235	-1923.250	-1923.260
32	Ge	Germanium			-2075.335	-2075.350	-2075.360
33	As	Arsenic			-2234.215	-2234.230	-2234.240
34	Se	Selenium			-2399.844	-2399.860	-2399.870
35	Br	Bromine			-2572.416	-2572.430	-2572.440
36	Kr	Krypton			-2752.029	-2752.040	-2752.050

TABLE I. Total energies in Hartree for the atom series from Helium to Krypton. Two columns with experimental data are given, EXP^(a) and EXP^(b), for details see Appendix F. Other columns show the total energies obtained by various methods (SIF, OEP and HF) within the exchange-only mode. The data are plotted in Fig. 9. In general, the SIF energies for the atom series lie slightly above the OEP ones, and both of them are higher than the HF results. The differences are discussed in the text.

as independent variables leading to energies lower than SIF where the orbitals are required to reproduce the density. This feature is further exemplified through the use of unconverged (and finite) basis set that leads to OEP energies similar to those of HF ³⁶.

C. Alternative Method

For special cases, e.g., closed shell atomic systems and generally spherical charge densities, Harbola and Sahni²⁹ have shown that the exchange potential can be obtained through the use of classical electrostatics. Notably, their method does not require the calculation of the susceptibility or its inverse and is independent of both SIF and OEP. For the case of Ar, the exchange potential found using their procedure precisely matches that which we find using the SIF approach (see Fig-

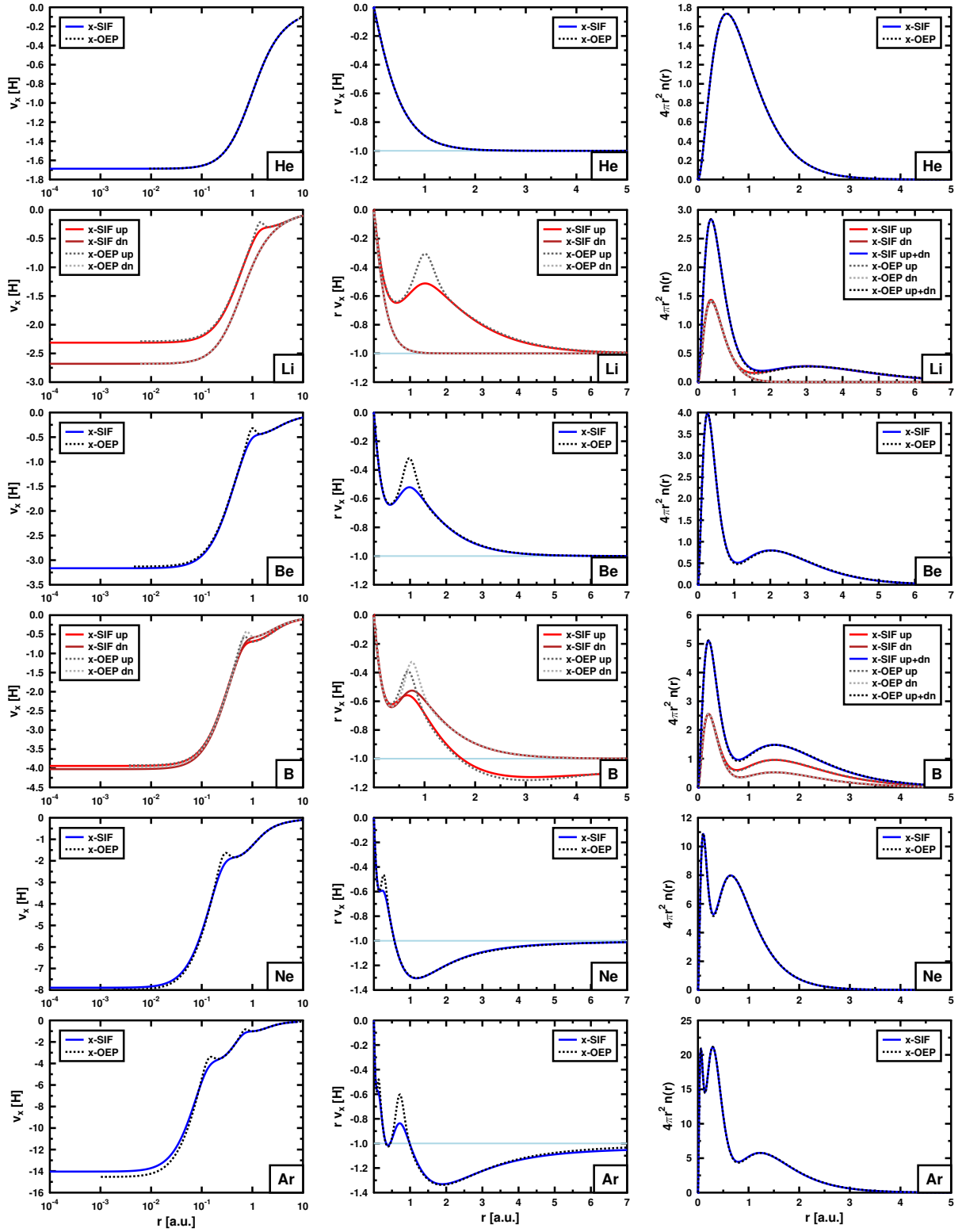


FIG. 7. Exchange potentials for Helium, Lithium, Beryllium, Boron, Neon and Argon. The left column depicts the radial exchange potential on a logarithmic scale, the middle column the exchange potential multiplied by r , the distance from the nucleus, so as to exhibit its asymptotic behavior, and the third column the density. Results of this paper (referred as x-SIF) are compared to OEP calculations. The curves represent self-consistent results obtained in the absence of a correlation energy (exchange only).

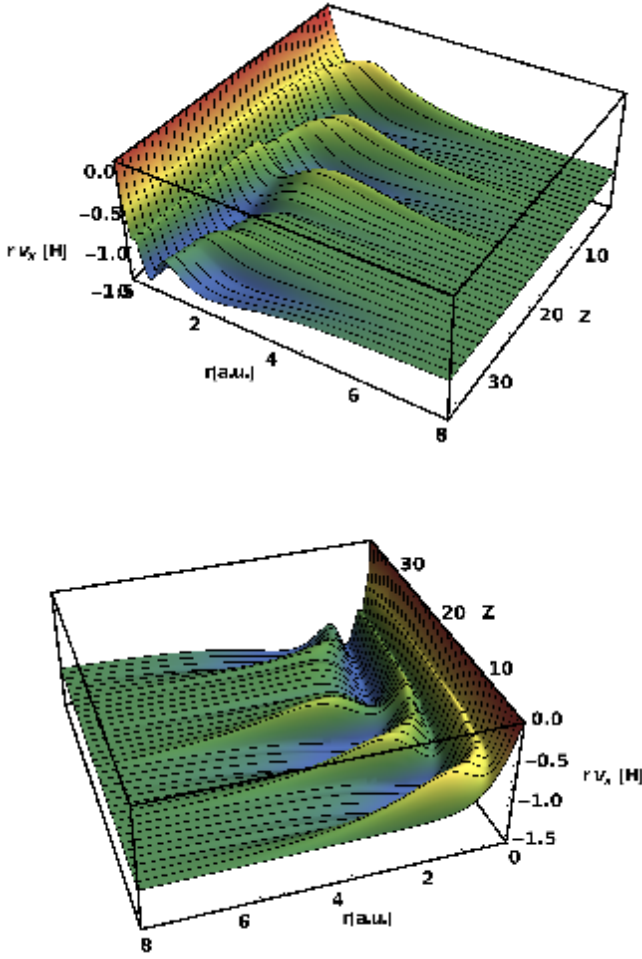


FIG. 8. SIF exchange potentials multiplied by r , the distance from the nucleus, for the atomic series Helium ($Z = 2$) to Krypton ($Z = 36$). Both figures show the same data, just at a different angle. The colored surface is for illustration, and exchange potentials are only meaningful for integer Z values, marked by the black lines.

ure 10). It is also noteworthy that Harbola and Sahni provide a physical interpretation of the negative slope of v_s obtained in some OEP calculations. It signifies the unphysical property that a negative charge, an electron, is repelled by a positive exchange hole.

In later work, Sahni^{37,38} states that the OEP results for the exchange potential are not the functional derivative of the exchange energy, but include an additional contribution to the energy, to which he refers as correlation-kinetic effects.

In still further work³⁹, Harbola and Sahni determined the ground-state energies of atomic systems from He to Rn. For closed shell systems, where densities are spherical, their results, that are exact in this case, coincide with our results shown in Table I and Fig. 10.

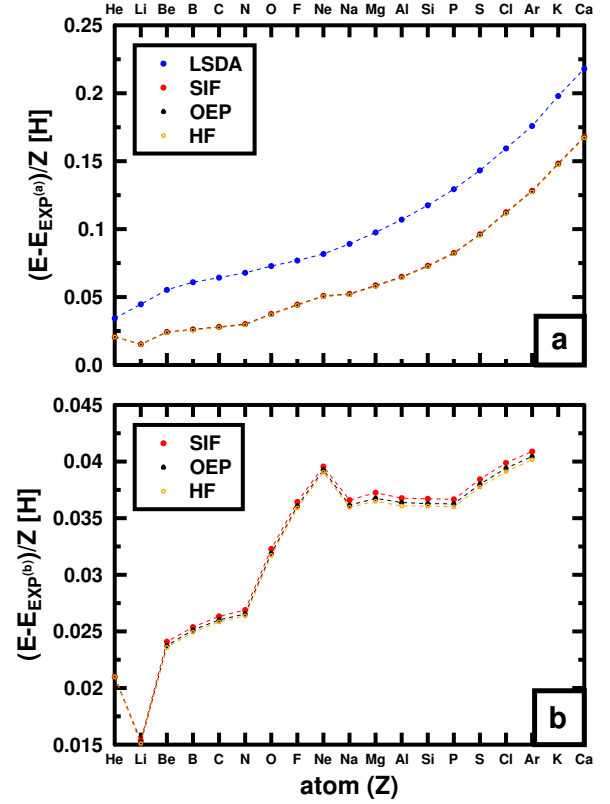


FIG. 9. Total energy differences, normalized by the number of electrons, between SIF, x-OEP, and HF to the experimental values, see Table I. a) refers to $\text{EXP}^{(a)}$, and b) to the column $\text{EXP}^{(b)}$. For comparison, LSDA energies³² are shown in panel a).

VI. CONCLUSIONS

The developments in the paper sprung from a particularly simple observation: The functional derivative of the Hartree term with respect to the density is facilitated by the explicit appearance of the density in the integrand. The same ease would materialize were the orbitals in the exchange term given explicitly in terms of the density in a differentiable functional form. The expansion of each orbital in the equidensity basis is particularly convenient for satisfying this requirement.

Based on this expansion, we have proposed a novel treatment for the Coulomb energy to be used in implementations of the KS formulation of DFT within a local approximation. In this treatment, the Coulomb energy is expressed in terms of the pair density constructed from the single-particle orbitals arising from the solution of the KS equations, thus avoiding by construction self-interaction effects. The pair density, in turn, is written in closed-form explicitly in terms of the density. This is accomplished through an expansion of the single-particle orbitals in terms of the equidensity basis whose elements are written explicitly in terms of the density. We have demonstrated how infinite sums appearing in the formalism can be replaced by quantities containing spatial derivatives

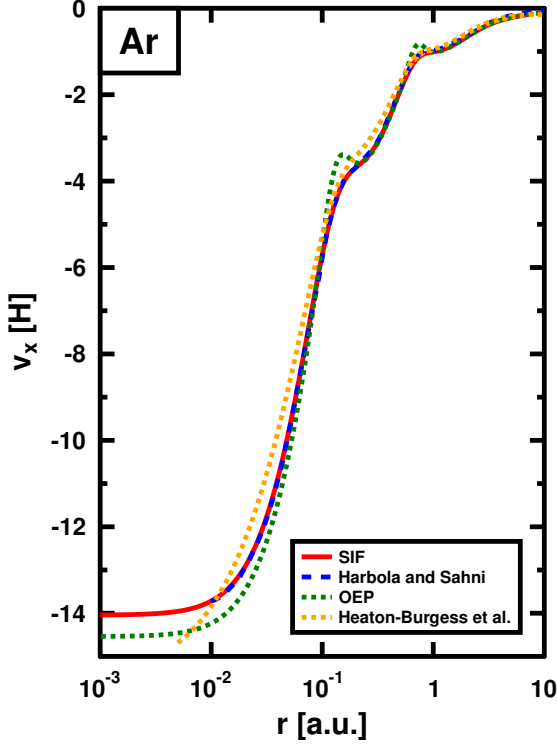


FIG. 10. Comparison between the exchange potential of Argon atom derived by the methods used in this paper (SIF, red, solid), the approach of Harbola and Sahni²⁹ (dashed, blue), and the results obtained by two different implementations of the OEP method, as indicated: OEP designates the results obtained within first order perturbation theory (dashed, green), and Heaton-Burgess et al.³⁵ (dashed, orange) those of directly varying the potential.

and can thus evaluate the sums (Eqn. (51) and (52)) to infinite order. The procedure is consistent with the bounds of DFT guaranteeing that the energies calculated within the method will be no lower than those of the true ground-state energy. In contrast to other methodologies directed at the determination of the exchange potential, such as the OEP, we find that the approach taken here is consistent with the fundamental premise of DFT: the only independent variable is the density, and it is the only variable with respect to which functional differentiation in principle can be performed.

We have shown that the SIF method provides a computational simple formalism to obtain the exchange potential as an upper bound of the energy, avoiding the calculation of the susceptibility and its inverse or the solution of an integral equation, where here only KS orbitals and their spatial derivatives are needed. Results for atomic systems are very close to those obtained by the OEP method and match the ones by Harbola and Sahni. In the form discussed in this paper, the formalism can immediately be applied to all non-periodic systems, e.g. molecules. An extension to periodic systems (solids) is currently the subject of ongoing work.

VII. ACKNOWLEDGMENTS

We are grateful to Stefan Kurth and Weitao Yang for providing their results of OEP calculations with which ours could be compared. We also gratefully acknowledge comments by X.-G. Zhang, Klaus Capelle, Hardy Gross and Virah Sahni. We thank as well Patrice E. A. Turchi for a careful and critical reading of the manuscript. The work at LLNL is supported by the U.S. DOE under Contract DE-AC52-07NA27344 with LLNS, LLC (MD, AG). Research at ORNL is sponsored by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences (DMN, GMS, MD), and the *Center for Defect Physics in Structural Materials (CDP)*, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (DMN, GMS, MD, AG).

Appendix A: Calculation of the integrals I^{ij}

In spherical coordinates, the integrals I^{ij} defined in Eq. (45) can be evaluated using the well known formula based on an expansion of U into spherical harmonics,

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{L=(l,m)} \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_L(\hat{r}) Y_L^*(\hat{r}'), \quad (\text{A1})$$

and

$$\begin{aligned} & \int_0^\infty dr' r'^2 g(r') \frac{r_{<}^l}{r_{>}^{l+1}} \\ &= \frac{1}{r^{l+1}} \int_0^r dr' r'^2 r'^l g(r') \\ & \quad + r^l \int_r^\infty dr' r'^2 r'^{-l-1} g(r'). \end{aligned} \quad (\text{A2})$$

In particular for a spherically symmetric function \bar{g} we get,

$$\int \frac{\bar{g}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \frac{4\pi}{r} \int_0^r \bar{g}(r') r'^2 dr' + 4\pi \int_r^\infty \bar{g}(r') r' dr'. \quad (\text{A3})$$

If the orbitals are of the form $f = R_L(r) Y_L(\theta, \phi)$ the angular part can be integrated analytically using the Gaunt coefficients,

$$C_{L'L''}^L = \int d\hat{r} Y_{L'}(\hat{r}) Y_{L''}^*(\hat{r}) Y_L(\hat{r}) \quad L = (l, m). \quad (\text{A4})$$

Then the integrals I^{ij} have the form,

$$I^{ij}(\mathbf{r}_1) = \sum_L^{L_{max}} R_L^{ij}(r_1) Y_L(\theta_1, \phi_1) \quad (\text{A5})$$

with $l_{max} = 2 \max(l_i, l_j)$ and

$$R_L^{ij}(r_1) = R_i^*(r_1) R_j(r_1) \left(C_{L_i, L_j}^L \right)^*, \quad (\text{A6})$$

where, depending on the symmetry, some coefficients R_L^{ij} might vanish. Since the functional derivatives of \mathbf{R} contain

δ distributions it will be difficult to expand them into a spherical harmonics basis. We find it more useful to evaluate the integrals I^{ij} in Cartesian coordinates and perform the remaining integrals to obtain the potential.

Appendix B: Derivatives of the transformed coordinates \mathbf{R}

1. Spatial Derivatives

For completeness, we provide all spatial derivatives of the functionals $\mathbf{R}(n(\mathbf{r}, [n]))$ defined in Eqs. (34).

$$\beta_{11} := \frac{\partial R_1}{\partial x} = 2\pi \frac{n(\mathbf{r})}{N(y, z)} \quad (\text{B1})$$

$$\beta_{12} := \frac{\partial R_1}{\partial y} = \frac{1}{N(y, z)} \left[2\pi \int_{-\infty}^x dx' \frac{\partial}{\partial y} n(x', y, z) - R_1 \int_{-\infty}^{\infty} dx' \frac{\partial}{\partial y} n(x', y, z) \right] \quad (\text{B2})$$

$$\beta_{13} := \frac{\partial R_1}{\partial z} = \frac{1}{N(y, z)} \left[2\pi \int_{-\infty}^x dx' \frac{\partial}{\partial z} n(x', y, z) - R_1 \int_{-\infty}^{\infty} dx' \frac{\partial}{\partial z} n(x', y, z) \right] \quad (\text{B3})$$

$$\beta_{21} := \frac{\partial R_2}{\partial x} = 0 \quad (\text{B4})$$

$$\beta_{22} := \frac{\partial R_2}{\partial y} = 2\pi \frac{N(y, z)}{N(z)} \quad (\text{B5})$$

$$\beta_{23} := \frac{\partial R_2}{\partial z} = \frac{1}{N(z)} \left[2\pi \int_{-\infty}^y dy' \int_{-\infty}^{\infty} dx' \frac{\partial}{\partial z} n(x', y', z) - R_2 \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' \frac{\partial}{\partial z} n(x', y', z) \right] \quad (\text{B6})$$

$$\beta_{31} := \frac{\partial R_3}{\partial x} = 0 \quad (\text{B7})$$

$$\beta_{32} := \frac{\partial R_3}{\partial y} = 0 \quad (\text{B8})$$

$$\beta_{33} := \frac{\partial R_3}{\partial z} = 2\pi \frac{N(z)}{N} \quad (\text{B9})$$

We see that the Jacobian is

$$\det \beta = \det \begin{vmatrix} \frac{\partial R_1}{\partial x} & \frac{\partial R_1}{\partial y} & \frac{\partial R_1}{\partial z} \\ 0 & \frac{\partial R_2}{\partial y} & \frac{\partial R_2}{\partial z} \\ 0 & 0 & \frac{\partial R_3}{\partial z} \end{vmatrix} = \frac{(2\pi)^3}{N} n(\mathbf{r}), \quad (\text{B10})$$

and in general $\det \beta = \frac{(2\pi)^d}{N} n(\mathbf{r})$ where d is the dimension of the system.

2. Functional Derivatives of the \mathbf{R}

Straightforward functional differentiations lead to the expressions:

$$\begin{aligned} \frac{\delta R_1(x, y, z, [n^\sigma])}{\delta n(\mathbf{r}'')} &= 2\pi \frac{\delta}{\delta n(\mathbf{r}'')} \frac{\int_{-\infty}^x dx' n(x', y, z, [n^\sigma])}{\int_{-\infty}^{\infty} dx' n(x', y, z, [n^\sigma])} \\ &= 2\pi \frac{\int_{-\infty}^x dx' \delta(x' - x'') \delta(y - y'') \delta(z - z'')}{\int_{-\infty}^{\infty} dx' n(x', y, z, [n^\sigma])} \\ &\quad - 2\pi \frac{\int_{-\infty}^{\infty} dx' \delta(x' - x'') \delta(y - y'') \delta(z - z'')}{\int_{-\infty}^{\infty} dx' n(x', y, z, [n^\sigma])} \\ &\quad \times \frac{\int_{-\infty}^x dx' n(x', y, z, [n^\sigma])}{\left[\int_{-\infty}^{\infty} dx' n(x', y, z, [n^\sigma]) \right]^2} \\ &= \frac{\delta(y - y'') \delta(z - z'')}{N(y, z, [n^\sigma])} \left[2\pi \Theta(x - x'') - R_1(x, y, z, [n^\sigma]) \right], \end{aligned}$$

$$\begin{aligned} \frac{\delta R_2(y, z, [n^\sigma])}{\delta n(\mathbf{r}'')} &= 2\pi \frac{\delta}{\delta n(\mathbf{r}'')} \frac{\int_{-\infty}^y dy' \int_{-\infty}^{\infty} dx' n(x', y', z, [n^\sigma])}{\int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' n(x', y', z, [n^\sigma])} \\ &= 2\pi \frac{\int_{-\infty}^y dy' \int_{-\infty}^{\infty} dx' \delta(x' - x'') \delta(y' - y'') \delta(z - z'')}{\int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' n(x', y', z, [n^\sigma])} \\ &\quad - 2\pi \frac{\int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' \delta(x' - x'') \delta(y' - y'') \delta(z - z'')}{\int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' n(x', y', z, [n^\sigma])} \\ &\quad \times \frac{\int_{-\infty}^y dy' \int_{-\infty}^{\infty} dx' n(x', y', z, [n^\sigma])}{\left[\int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' n(x', y', z, [n^\sigma]) \right]^2} \end{aligned}$$

$$= \frac{\delta(z - z'')}{N(z, [n^\sigma])} \left[2\pi \Theta(y - y'') - R_2(y, z, n[\sigma]) \right],$$

and

$$\begin{aligned} \frac{\delta R_3(z, [n^\sigma])}{\delta n(\mathbf{r}'')} &= 2\pi \frac{\delta}{\delta n(\mathbf{r}'')} \frac{\int_{-\infty}^z dz' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' n(x', y', z', [n^\sigma])}{\int_{-\infty}^{\infty} dz' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' n(x', y', z', [n^\sigma])} \\ &= 2\pi \frac{\int_{-\infty}^z dz' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' \delta(x' - x'') \delta(y' - y'') \delta(z' - z'')}{\int_{-\infty}^{\infty} dz' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' n(x', y', z', [n^\sigma])} \\ &\quad - 2\pi \frac{\int_{-\infty}^{\infty} dz' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' \delta(x' - x'') \delta(y' - y'') \delta(z' - z'')}{\int_{-\infty}^{\infty} dz' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' n(x', y', z', [n^\sigma])} \\ &\quad \times \frac{\int_{-\infty}^z dz' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' n(x', y', z', [n^\sigma])}{\left[\int_{-\infty}^{\infty} dz' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dx' n(x', y', z', [n^\sigma]) \right]^2} \\ &= \frac{1}{N^\sigma} \left[2\pi \Theta(z - z'') - R_3(z, n[\sigma]) \right]. \end{aligned}$$

Appendix C: Spatial Derivatives and their Connection to Infinite Sums

The use of the equidensity basis requires the evaluation of the rather difficult infinite sum in Eq. (50) whose value depends on the number of terms taken into account. The following considerations allow the sum to be carried out to infinite order.

First, we discuss the one-dimensional case. We are interested in evaluating the sum,

$$\sum_k a_k i k \phi_k(x, [n^\sigma]) = \sum_k a_k i k \sqrt{\frac{n^\sigma(x)}{N^\sigma}} e^{i k q(x, [n^\sigma])}, \quad (\text{C1})$$

where the orbitals $f(x)$ are expressed in the form (where for simplicity of notation we omit the spin superscript on the orbitals),

$$f(x) = \sum_k a_k \phi_k = \sum_k a_k \sqrt{\frac{n^\sigma(x)}{N^\sigma}} e^{i k q(x, [n^\sigma])}. \quad (\text{C2})$$

From the definition,

$$q(x, [n^\sigma]) = \frac{2\pi}{N^\sigma} \int_{x_0}^x n^\sigma(x') dx' \quad (\text{C3})$$

we have,

$$\frac{\delta q(x, [n^\sigma])}{\delta n^\sigma(x')} = \frac{2\pi}{N^\sigma} \Theta(x - x'), \quad (\text{C4})$$

and

$$\frac{dq(x, [n^\sigma])}{dx} = \frac{2\pi}{N^\sigma} n^\sigma(x). \quad (\text{C5})$$

The spatial derivative is given by

$$f' = \frac{df(x)}{dx}$$

$$= \sum_k a_k \frac{d}{dx} \left(\sqrt{\frac{n^\sigma(x)}{N^\sigma}} e^{i k q(x, [n^\sigma])} \right) \quad (\text{C6})$$

$$\begin{aligned} &= \sum_k \left[\frac{1}{\sqrt{N^\sigma}} a_k \frac{1}{2\sqrt{n^\sigma(x)}} \frac{dn^\sigma(x)}{dx} e^{i k q(x, [n^\sigma])} \right. \\ &\quad \left. + i k a_k \sqrt{\frac{n^\sigma(x)}{N^\sigma}} e^{i k q(x, [n^\sigma])} \frac{dq(x)}{dx} \right] \\ &= \frac{n^{\sigma'}(x)}{2n^\sigma(x)} \underbrace{\sum_k a_k \sqrt{\frac{n^\sigma(x)}{N^\sigma}} e^{i k q(x, [n^\sigma])}}_{f(x)} \\ &\quad + \underbrace{\frac{2\pi}{N^\sigma} n^\sigma(x)}_{q'} \sum_k a_k i k \sqrt{\frac{n^\sigma(x)}{N^\sigma}} e^{i k q(x, [n^\sigma])}, \quad (\text{C7}) \end{aligned}$$

from which it follows that

$$\begin{aligned} &\sum_k a_k i k \sqrt{\frac{n^\sigma(x)}{N^\sigma}} e^{i k q(x, [n^\sigma])} \\ &= \frac{N^\sigma}{2\pi n^\sigma(x)} \frac{df(x)}{dx} - \frac{N^\sigma}{4\pi [n^\sigma(x)]^2} f(x) \frac{dn^\sigma(x)}{dx} \\ &= \frac{N^\sigma}{2\pi n^\sigma(x)} \left[f' - \frac{1}{2n^\sigma(x)} f(x) n^{\sigma'} \right] \quad (\text{C8}) \end{aligned}$$

$$= \frac{N^\sigma}{2\pi n^\sigma(x)} \left[\sqrt{n^\sigma(x)} \left(\frac{f(x)}{\sqrt{n^\sigma(x)}} \right)' \right] \quad (\text{C9})$$

$$= \frac{N^\sigma}{2\pi} \frac{1}{\sqrt{n^\sigma(x)}} \left(\frac{f(x)}{\sqrt{n^\sigma(x)}} \right)' \quad (\text{C10})$$

The spatial derivatives with respect to x (marked by primes) of the orbitals and the density can be calculated numerically.

It now follows that it is no longer necessary to construct explicitly the equidensity basis, or the expansion coefficients, a_k . The three-dimensional generalization of the one-

dimensional results is straightforward. The components of the gradient of an orbital, f , decomposed into the equidensity basis are given by

$$\nabla_\alpha f = \sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \frac{\partial}{\partial \alpha} \left(\sqrt{\frac{n^\sigma(\mathbf{r})}{N^\sigma}} e^{i \mathbf{k} \cdot \mathbf{R}(\mathbf{r}, [n^\sigma])} \right) \quad (\text{C11})$$

$$= \frac{1}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial \alpha} f(\mathbf{r}) + i \sum_{\mathbf{k}} \phi_{\mathbf{k}}^\sigma(\mathbf{r}, [n^\sigma]) \left(\frac{\partial \mathbf{R}(\mathbf{r}, [n^\sigma])}{\partial \alpha} \cdot \mathbf{k} \right), \quad (\text{C12})$$

with $\alpha = \{x, y, z\}$.

From Eqs. (C12), (B1), (B4) and (B7) we obtain

$$\nabla_x f = \frac{1}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial x} f(\mathbf{r}) + \sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_1) \underbrace{\left(2\pi \frac{n^\sigma(\mathbf{r})}{N^\sigma(y, z)} \right)}_{\beta_{11}}, \quad (\text{C13})$$

and

$$Q_x^\sigma = \sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_1) = \frac{N^\sigma(y, z)}{2\pi n^\sigma(\mathbf{r})} \times \left[\nabla_x f - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial x} \right]. \quad (\text{C14})$$

In the same way, using Eqs. (C12), (B2), (B5) and (B8)

$$\nabla_y f = \frac{1}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial y} f(\mathbf{r}) + \sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_1) \beta_{12}^\sigma + \sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_2) \underbrace{2\pi \frac{N^\sigma(y, z)}{N^\sigma(z)}}_{\beta_{22}}, \quad (\text{C15})$$

we obtain the expression,

$$Q_y^\sigma = \sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_2) = \frac{N^\sigma(z)}{2\pi N^\sigma(y, z)} \times \left[\nabla_y f - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial y} - Q_x^\sigma \beta_{12}^\sigma \right]. \quad (\text{C16})$$

Finally using Eqs. (C12), (B3), (B6) and (B9), we find,

$$\nabla_z f = \frac{1}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial z} f(\mathbf{r}) + \sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_1) \beta_{13}^\sigma + \sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_2) \beta_{23}^\sigma + \sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_3) \underbrace{2\pi \frac{N^\sigma(z)}{N^\sigma}}_{\beta_{33}}, \quad (\text{C17})$$

and

$$Q_z^\sigma = \sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_3) = \frac{N^\sigma}{2\pi N^\sigma(z)} \times \left[\nabla_z f - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial z} - Q_x^\sigma \beta_{13}^\sigma - Q_y^\sigma \beta_{23}^\sigma \right]. \quad (\text{C18})$$

These results can be summarized in vector form,

$$\sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(i\mathbf{k}) =: \begin{pmatrix} Q_x^\sigma \\ Q_y^\sigma \\ Q_z^\sigma \end{pmatrix} = \begin{pmatrix} \frac{N^\sigma(y, z)}{2\pi n^\sigma(\mathbf{r})} \left[\nabla_x f - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial x} \right] \\ \frac{N^\sigma(z)}{2\pi N^\sigma(y, z)} \left[\nabla_y f - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial y} - Q_x^\sigma \beta_{12}^\sigma \right] \\ \frac{N^\sigma}{2\pi N^\sigma(z)} \left[\nabla_z f - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial z} - Q_x^\sigma \beta_{13}^\sigma - Q_y^\sigma \beta_{23}^\sigma \right] \end{pmatrix}.$$

Appendix D: Numerical Evaluation of the Exchange Potential Components

We split the exchange potential into different components with regard to Eqn. (54) and (47)

$$v_x^\sigma(\mathbf{r}') = v_x^{\sigma[1]}(\mathbf{r}') + v_x^{\sigma[\text{Qx}]}(\mathbf{r}') + v_x^{\sigma[\text{Qy}]}(\mathbf{r}') + v_x^{\sigma[\text{Qz}]}(\mathbf{r}'). \quad (\text{D1})$$

In the following we show how to evaluate the different integrals to obtain the exchange potential, in cartesian coordinates, which makes it easy to deal with integrals over Theta functions.

The contribution from the first term of Eq. (54) takes the form,

$$v_x^{\sigma[1]}(\mathbf{r}') = -2\Re \sum_{ij} \delta_{\sigma_i, \sigma_j, \sigma} \times \int d\mathbf{r}_1 I^{ij}(\mathbf{r}_1) f_j^*(\mathbf{r}_1) f_i(\mathbf{r}_1) \frac{\delta(\mathbf{r}_1 - \mathbf{r}')}{2n^\sigma(\mathbf{r}_1)} = -\frac{1}{n^\sigma(\mathbf{r}')} \Re \sum_{ij} \delta_{\sigma_i, \sigma_j, \sigma} I^{ij}(\mathbf{r}') f_j^*(\mathbf{r}') f_i(\mathbf{r}').$$

The contribution that includes $\left(\frac{\partial R_1}{\partial n} Q_x\right)$ in the last term of Eq. (54), reads as follows

$$v_x^{\sigma[\text{Qx}]}(\mathbf{r}') = -2\Re \sum_{ij} \delta_{\sigma_i, \sigma_j, \sigma} \int d\mathbf{r} I^{ij}(\mathbf{r}) f_j^*(\mathbf{r}) \frac{\delta(y - y') \delta(z - z')}{N^\sigma(y, z, [n])} \times \left[2\pi \Theta(x - x') - R_1(x, y, z, [n^\sigma]) \right] \times \frac{N^\sigma(y, z)}{2\pi n^\sigma(\mathbf{r})} \times \left[\nabla_x f_i - \frac{f_i(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial x} \right] = -2\Re \int dx dy dz \left\{ \left[2\pi \Theta(x - x') - R_1(x, y, z, [n^\sigma]) \right] \times \right.$$

$$\left[\sum_{ij} \delta_{\sigma_i, \sigma_j, \sigma} I^{ij}(x, y, z) f_j^*(x, y, z) \frac{Q_x^i(x, y, z)}{N^\sigma(y, z)} \right] \times \delta(y - y') \delta(z - z') \Big\}. \quad (\text{D2})$$

The integrals over y and z are trivial. Left over are two simple integral over x .

We can define:

$$\begin{aligned} A_x^\sigma(x, y, z) &:= \sum_{ij} \delta_{\sigma_i, \sigma_j, \sigma} I^{ij}(x, y, z) f_j^*(x, y, z) \frac{Q_x^i(x, y, z)}{N^\sigma(y, z)} \\ A_y^\sigma(x, y, z) &:= \sum_{ij} \delta_{\sigma_i, \sigma_j, \sigma} I^{ij}(x, y, z) f_j^*(x, y, z) \frac{Q_y^i(x, y, z)}{N^\sigma(z)} \\ A_z^\sigma(x, y, z) &:= \sum_{ij} \delta_{\sigma_i, \sigma_j, \sigma} I^{ij}(x, y, z) f_j^*(x, y, z) \frac{Q_z^i(x, y, z)}{N^\sigma}, \end{aligned}$$

that leads to

$$\begin{aligned} v_x^{\sigma[\text{QX}]}(\mathbf{r}') &= v_x^{\sigma[\text{QX}]}(x', y', z') \\ &= -2\Re \left[\int_{x'}^\infty dx \, 2\pi A_x^\sigma(x, y', z') \right. \\ &\quad \left. - \int_{-\infty}^\infty dx \, R_1(x, y', z', [n^\sigma]) A_x^\sigma(x, y', z') \right]. \quad (\text{D3}) \end{aligned}$$

The contribution from the term that includes $(\frac{\partial R_2}{\partial n} Q_y)$ in the last term of equation (54), reads as follows

$$\begin{aligned} v_x^{\sigma[\text{QY}]}(\mathbf{r}') &= v_x^{\sigma[\text{QY}]}(y', z') \\ &= -2\Re \int dx \, dy \, dz \left\{ \left[2\pi \Theta(y - y') - R_2(y, z, [n^\sigma]) \right] \times \right. \\ &\quad \left[\sum_{ij} \delta_{\sigma_i, \sigma_j, \sigma} I^{ij}(x, y, z) f_j^*(x, y, z) \frac{Q_y^i(x, y, z)}{N^\sigma(z)} \right] \times \\ &\quad \left. \delta(z - z') \right\} \quad (\text{D4}) \\ &= -2\Re \left[\int_{y'}^\infty dy \int_{-\infty}^\infty dx \, 2\pi A_y^\sigma(x, y, z') \right. \\ &\quad \left. - \int_{-\infty}^\infty dy \int_{-\infty}^\infty dx \, R_2(y, z', [n^\sigma]) A_y^\sigma(x, y, z') \right]. \quad (\text{D5}) \end{aligned}$$

The contribution from the term that includes $(\frac{\partial R_3}{\partial n} Q_z)$ in the last term of equation (54), reads as follows

$$\begin{aligned} v_x^{\sigma[\text{QZ}]}(\mathbf{r}') &= v_x^{\sigma[\text{QZ}]}(z') \\ &= -2\Re \int dx \, dy \, dz \left\{ \left[2\pi \Theta(z - z') - R_3(z, [n^\sigma]) \right] \times \right. \\ &\quad \left[\sum_{ij} \delta_{\sigma_i, \sigma_j, \sigma} I^{ij}(x, y, z) f_j^*(x, y, z) \frac{Q_z^i(x, y, z)}{N^\sigma} \right] \Big\} \end{aligned}$$

$$\begin{aligned} &= -2\Re \left[\int_{z'}^\infty dz \int_{-\infty}^\infty dy \int_{-\infty}^\infty dx \, 2\pi A_z^\sigma(x, y, z) \right. \\ &\quad \left. - \underbrace{\int_{-\infty}^\infty dz \int_{-\infty}^\infty dy \int_{-\infty}^\infty dx R_3(z, [n^\sigma]) A_z^\sigma(x, y, z)}_{\text{this is a constant, spin dependent}} \right]. \quad (\text{D6}) \end{aligned}$$

Appendix E: Functional Derivative of the Hartree term

For the Hartree term it is easy to show that

$$\frac{\delta U_H}{\delta n^\uparrow(\mathbf{r})} = \frac{\delta U_H}{\delta n^\downarrow(\mathbf{r})} = \frac{\delta U_H}{\delta n(\mathbf{r})} = V_H(\mathbf{r}). \quad (\text{E1})$$

Nevertheless, it still needs to be proven that the proposed procedure calculating the functional derivative with respect to the density leads to the exact same result, namely the Hartree potential.

For the spin density we have

$$n^\sigma(\mathbf{r}) = \sum_i^{N^\sigma} f_i^*(\mathbf{r}) f_i(\mathbf{r}) \quad (\text{E2})$$

$$\nabla_\alpha n^\sigma(\mathbf{r}) = \sum_i^{N^\sigma} [f_i^*(\mathbf{r}) \nabla_\alpha f_i(\mathbf{r}) + f_i(\mathbf{r}) \nabla_\alpha f_i^*(\mathbf{r})] \quad (\text{E3})$$

where $\alpha \in \{x, y, z\}$ and the sum runs over all orbitals of spin σ . In the spin polarized case there is no functional dependency of an orbital with spin σ and the spin density with the opposite spin.

$$\frac{\delta f_i^\uparrow}{\delta n^\downarrow} = 0 = \frac{\delta f_i^\downarrow}{\delta n^\uparrow} \quad (\text{E4})$$

Now we can show that the following expression vanishes (here shown for $\sigma = \uparrow$):

$$\sum_i^{\uparrow \text{only}} \left\{ f_i^* \left[\nabla_\alpha f_i - \frac{f_i}{2n} \frac{\partial n^\sigma}{\partial \alpha} \right] + f_i \left[\nabla_\alpha f_i^* - \frac{f_i^*}{2n} \frac{\partial n^\sigma}{\partial \alpha} \right] \right\} \quad (\text{E5})$$

$$\begin{aligned} &= \sum_i^{\uparrow \text{only}} [f_i^* \nabla_\alpha f_i + f_i(\mathbf{r}) \nabla_\alpha f_i^*] - \nabla_\alpha n^\sigma \sum_i^{\uparrow \text{only}} \frac{f_i^* f_i}{n^\sigma} \\ &= \frac{\partial n^\sigma}{\partial \alpha} - \frac{\partial n^\sigma}{\partial \alpha} = 0 \quad (\text{E6}) \end{aligned}$$

This leads directly to:

$$\begin{aligned} \sum_i^{N^\sigma} f_i Q_x^{i*} + f_i^* Q_x^i &= 0 \\ \sum_i^{N^\sigma} f_i Q_y^{i*} + f_i^* Q_y^i &= 0 \\ \sum_i^{N^\sigma} f_i Q_z^{i*} + f_i^* Q_z^i &= 0, \quad (\text{E7}) \end{aligned}$$

showing that there is no contribution to the potential from the term appearing in the functional derivative of an orbital with respect to the density $\frac{\delta \mathbf{R}[n(\mathbf{r})]}{\delta n(\mathbf{r}')} \cdot \sum_{\mathbf{k}} a_{\mathbf{k}}^i i \mathbf{k} \phi_{\mathbf{k}}[n(\mathbf{r})]$ $= \frac{\delta \mathbf{R}[n(\mathbf{r})]}{\delta n(\mathbf{r}')} \cdot \mathbf{Q}$. The remaining four terms used to calculate the potential contribution have the same structure,

$$\frac{1}{2} \sum_{ij} \int \int d\mathbf{r}_1 d\mathbf{r}_2 U(\mathbf{r}_1, \mathbf{r}_2) \times f_j^*(\mathbf{r}_2) f_i(\mathbf{r}_1) f_j(\mathbf{r}_2) \frac{f_i^*(\mathbf{r}_1)}{2n^\sigma(\mathbf{r}')} \delta(\mathbf{r}_1 - \mathbf{r}') \delta_{\sigma_i, \sigma} \quad (\text{E8})$$

$$= \frac{1}{2} \sum_i \delta_{\sigma_i, \sigma} \frac{f_i(\mathbf{r}') f_i^*(\mathbf{r}')}{2n^\sigma(\mathbf{r}')} \int d\mathbf{r}_2 U(\mathbf{r}_1, \mathbf{r}') \sum_j f_j(\mathbf{r}_2) f_j^*(\mathbf{r}_2) \\ = \frac{1}{2} \frac{1}{2} \int d\mathbf{r}_2 U(\mathbf{r}', \mathbf{r}_2) n(\mathbf{r}_2) = \frac{1}{4} V^H(\mathbf{r}'). \quad (\text{E9})$$

Due to the product rule during the functional differentiation this term appears four times so that the contribution to the potential is exactly the Hartree potential. One should note that taking the functional derivative with respect to the spin-up or spin-down density leads to the same result. All the above relationships apply in the same way in the non-spin polarized case.

We have now proven that the proposed procedure to calculate the functional derivative of the Hartree term leads exactly to the Hartree potential.

Appendix F: Experimental Data for the Atom Series

In practice, it is not easy and in most cases impossible to measure quantities corresponding to the total energy of calculations. In principle, one has to ionize all electrons and measure the energy. The total energy is then the sum of all ionization energies. For the first few atoms of the periodic table this seems to be possible, but with larger Z it becomes harder and harder to ionize all of the electrons. A complete set of wavelength corresponding to all of the ionization potentials from Hydrogen to Calcium ($Z = 20$) has been published⁴⁰ quite some time ago. One can now use the CODATA^{41,42}, containing the latest values of physical constants and their errors, to convert the measured wave length to energies. The second column of Table I labeled EXP^(a) contains these data, with the estimated error bars.

Based on the experimental data⁴⁰ some effort has been made to try to calculate non-relativistic correlation energies and relativistic corrections to the ionization potentials^{30,43}. The data from reference³⁰ seems to be widely used in the literature. But since they were determined by calculations rather than measurements, or only partially, we have doubts that these energies can be quoted as experimental data. Because it is not clear which data set should be used, we decided to quote both in this paper.

- ¹ P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- ² W. Kohn and P. Vashista, *Theory of the Inhomogeneous Electron Gas* (Edited by S. Lundquist and N. H. March), Physics of Solids and Liquid Series (Plenum Press, New York, 1983).
- ³ R. G. Parr and C. Y. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).
- ⁴ R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer Verlag, Berlin, New York, 1990).
- ⁵ W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ⁶ S. Kurth and S. Pittalis, in *Computational Nanoscience: Do It Yourself!*, NIC Series Volume 31, edited by J. Groten-dorst, S. Blügel, and D. Marx, Forschungszentrum Jülich (Forschungszentrum Jülich, 2006) pp. 299–334, ISBN 3-00-017350-1.
- ⁷ S. Kümmel and L. Kronik, *Rev. Mod. Phys.* **80**, 3 (2008).
- ⁸ J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981), and discussion therein. This paper provides a clear delineation of the self-interaction effects and describes a formal approach that can be used to correct for them.
- ⁹ A. Svane and O. Gunnarsson, *Phys. Rev. Lett.* **65**, 1148 (1990).
- ¹⁰ A. Svane, L. Petit, Z. Szotek, and W. M. Temmerman, *Phys. Rev. B* **76**, 115116 (2007).
- ¹¹ P. Mori-Sánchez, A. J. Cohen, and W. Yang, *J. Chem. Phys.* **124**, 091102 (2006).
- ¹² W. Yang and Q. Wu, *Phys. Rev. Lett.* **89**, 143002 (2002).
- ¹³ C. Fiolhais, F. Nogueira, and M. A. Marques, eds., *Lecture Notes in Physics*, Lecture Notes in Physics, Vol. 620 (Springer, Berlin, Heidelberg, New York, 2003).
- ¹⁴ E. Engel, in *A Primer in Density Functional Theory*, Lecture Notes in Physics, Vol. 620, edited by C. Fiolhais, F. Nogueira, and M. A. Marques (Springer, Berlin, Heidelberg, New York, 2003) Chap. 2, pp. 56–122, ISBN 978-3-540-03083-6.
- ¹⁵ J. D. Talman and W. F. Shadwick, *Phys. Rev. A* **14**, 36 (1976).
- ¹⁶ S. Kümmel and J. P. Perdew, *Phys. Rev. Lett.* **90**, 043004 (2003).
- ¹⁷ J. B. Krieger, Y. Li, and G. J. Iafrate, *Phys. Rev. A* **46**, 5453 (1992).
- ¹⁸ LibXC, www.tddft.org/programs/octopus/wiki/index.php/Libxc:manual.
- ¹⁹ Q. Wu and W. Yang, *The Journal of Chemical Physics* **118**, 2498 (2003).
- ²⁰ A. Gonis, M. Däne, D. Nicholson, and G. Stocks, *Solid State Communications* **152**, 771 (2012).
- ²¹ M. Levy, *Proceedings of the National Academy of Sciences* **76**, 6062 (1979), <http://www.pnas.org/content/76/12/6062.full.pdf+html>.
- ²² E. H. Lieb, in *Physics as Natural Philosophy, Essays in Honor of Laszlo Tisza*, edited by A. Shimony and H. Feshbach (MIT Press Cambridge, Massachusetts, 1982) See also, E. H. Lieb, in *density Functional methods in Physics*, ed. R. M. Dreizler, NATO ASI Series B123, (Plenum, New York, 1985) p.31.
- ²³ J. Cioslowski, *Phys. Rev. Lett.* **60**, 2141 (1988).
- ²⁴ D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- ²⁵ W. Macke, *Annalen der Physik* **452**, 1 (1955), 6. Folge, Band 17, Heft 1.
- ²⁶ J. E. Harriman, *Phys. Rev. A* **24**, 680 (1981).
- ²⁷ G. Zumbach and K. Maschke, *Phys. Rev. A* **28**, 544 (1983).
- ²⁸ E. V. Ludefia and R. Lopez-Boada, in *Topics in Current Chemistry 180: Density Functional Theory I, Functionals and Effective Potentials*, Topics in Current Chemistry, Vol. 180, edited by R. F. Nalewajski (Springer Verlag Berlin Heidelberg New York, 1996) Topics in Current Chemistry ed., pp. 169–224, ISBN 3-540-

- 61091-X.
- ²⁹ M. K. Harbola and V. Sahni, *Phys. Rev. Lett.* **62**, 489 (1989).
 - ³⁰ S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia, and C. F. p Fischer, *Phys. Rev. A* **47**, 3649 (1993).
 - ³¹ Y. Li, J. B. Krieger, and G. J. Iafrate, *Phys. Rev. A* **47**, 165 (1993).
 - ³² NIST, Atomic Reference Data for Electronic Structure Calculations, <http://physics.nist.gov/PhysRefData/DFTdata/Tables/ptable.html>.
 - ³³ S. Hirata, S. Ivanov, I. Grabowski, R. J. Bartlett, K. Burke, and J. D. Talman, *The Journal of Chemical Physics* **115**, 1635 (2001).
 - ³⁴ C. R. Jacob, *The Journal of Chemical Physics* **135**, 244102 (2011).
 - ³⁵ T. Heaton-Burgess, F. A. Bulat, and W. Yang, *Phys. Rev. Lett.* **98**, 256401 (2007).
 - ³⁶ V. N. Staroverov, G. E. Scuseria, and E. R. Davidson, *The Journal of Chemical Physics* **124**, 141103 (2006).
 - ³⁷ V. Sahni, *Quantal Density Functional Theory* (Springer, 2004).
 - ³⁸ V. Sahni, *Quantal Density Functional Theory II* (Springer, 2009).
 - ³⁹ V. Sahni, Y. Li, and M. K. Harbola, *Phys. Rev. A* **45**, 1434 (1992).
 - ⁴⁰ C. E. Moore, *Ionization Potentials and Ionization Limits Derived from the Analysis of Optical Spectra*, NSRDS-NBS 34 (Unites States Department of Commerce, National Bureau of Standards, Office of Standard Reference Data, National Bureau of Standards, Washington, D.C. 20234, 1970).
 - ⁴¹ P. J. Mohr, B. N. Taylor, and D. B. Newell, *Rev. Mod. Phys.* **80**, 633 (2008).
 - ⁴² P. J. Mohr, B. N. Taylor, and D. B. Newell, *J. Phys. Chem. Ref. Data* **37**, 1187 (2008).
 - ⁴³ E. R. Davidson, S. A. Hagstrom, S. J. Chakravorty, V. M. Umar, and C. F. Fischer, *Phys. Rev. A* **44**, 7071 (1991).